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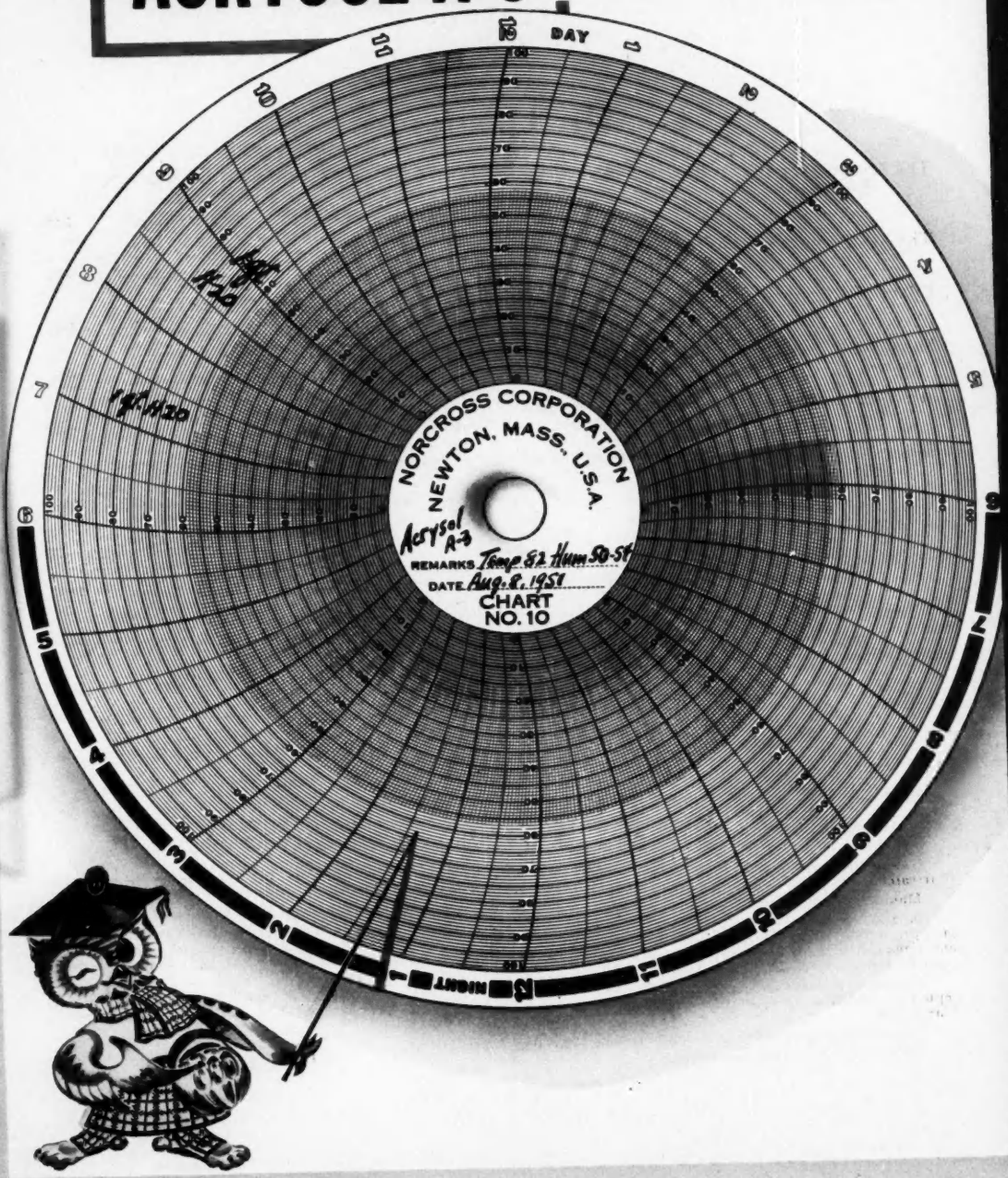

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re. DISCONTINUANCE of
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The monthly mailing, under separate cover, to subscribers of TEXTILE RESEARCH JOURNAL of copies of the textile abstracts prepared by The Textile Institute of Great Britain will be discontinued at the close of this year (1951). The December issue will be the final copy to be mailed.

The British Abstracts appear monthly in *The Journal of The Textile Institute*, and may be obtained through subscription to that journal by writing to The Textile Institute, 10 Blackfriars St., Manchester 3, England.

In terminating the special arrangement with the British Institute, it is felt that the annual "Review of Textile Research and Development" prepared by the staff of Textile Research Institute constitutes a service of greater value to the industry. Commencing with the calendar year 1949, these reviews have appeared in the May, 1950, and May, 1951, issues of TEXTILE RESEARCH JOURNAL. The review for the calendar year 1950 contained a bibliography of 1,622 references, and included a discussion of important contributions to progress in research and manufacturing developments. A limited number of reprints of the reviews for 1949 and 1950 are still available and can be obtained without charge.

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TEXTILE RESEARCH JOURNAL

VOL. XXI, No. 12 December, 1951

The Measurement and Physical Interpretation of the Mechanical Strength of Filaments*

Waller George†

Naval Research Laboratory, Washington, D. C.

Introduction

The mechanical strength of a solid is usually estimated in terms of the loads required to produce arbitrary amounts of deformation. One may plot the loads and associated deformations obtainable from a given experimental procedure as a curve which is the locus of all such possible strength values. When the loads and deformation measures are suitably normalized, this locus becomes the so-called stress-strain relation. In general, experiments which yield load and deformation measures are more or less sensitive to the thermal and chemical character of the media surrounding the material under study. If the surrounding medium is controlled as to its chemical and physical state, there are two simple and mutually exclusive types of experiment possible which can be performed to yield a stress-strain relation. One type involves controlled loading, the other controlled deformation.

In the present discussion of mechanical strength, similarities between fiber-forming materials are stressed. It is suggested that many of the macro mechanical properties of filamentous solids can be related in a remarkably simple way to the geometric and dynamic properties of micro domains existing within the filaments. These micro domains are characterized by elements of length which are large compared with the interatomic distances within the solid, but probably are quite small compared with the cross-sectional dimensions of the filament. Every attempt is made to support the thesis with factual data, but it should be noted that the subject is still in the development stage; hence, many fine points and interlinking arguments may require modification in the light of future work. It is thought, however, that the discussion will prove valuable in illustrating a somewhat new point of view, a possible approach to the often bewildering and always complex problems of fiber strength.

The subject matter is conveniently divided into two parts: the first is concerned with the macro- and microscopic evidence for the existence of structural domains within filaments; the second is concerned with the results of selected experiments which find a ready interpretation in terms of the static and dynamic properties of these domains.

Discussion of the limitations imposed on the mechanical strength of solids by structural arrangements characterized by a length measure is not completely new. The literature on the physics of the strength of solids published during the past 25 years contains examples of this type of discussion [10, 12, 32, 36]. Unfortunately, many of these works dealt with highly specialized subject matter and are not widely known. A discussion of the mechanical strength of filaments in particular in terms of domain concepts is relatively new. There are many terms which have been used to characterize the

* This paper, in essentially the present form, was read before the Fall Meeting of The Fiber Society at the Lowell Textile Institute, Lowell, Mass., September 8, 1949.

† Mechanics Division.

domains dealt with herein; probably the first was "mosaic block," which was used by Zwicky [36] in a discussion of the strength of ionic crystals such as rock salt and silver chloride. Later, "crystallite," "microcrystal," "micelle," and other terms were introduced in similar circumstances. Unfortunately, all of these terms have highly select and special meanings in technical fields quite foreign to that of the physics of solids.

Regardless of the term used, what is essential to the discussion of the physics of mechanical strength is the recognition that solids in general do not exist in macroscopic dimensions as simple repetitions of elementary atomic configurations, but possess an intermediate structure which can be thought of as constructed in a relatively perfect fashion from the repetition of elementary atomic configurations (unit cells). This elementary configuration can be that of the simple cubic lattice exhibited by many ionic crystals, or the somewhat lower symmetry of body and face centered cubic technical metals, or the yet lower symmetry of crystallized high-polymeric materials which are of technical importance as synthetic fibers. Regardless of elementary microscopic structural class, there seems to be an abundance of data of a variety of types pointing to the existence of one or more types of intermediate structures which can exist in the solid state. Examples of such intermediate structures are grains in metals, crystallites and micelles in natural fibers, internal stress or strain gradients, free surfaces and grain boundaries.

The term "domain" is used herein to refer to an intermediate structural configuration which is characterized by dimensions intermediate between the macroscopic and microscopic* dimensions of the solid. One goal of studies of these domains is the determination of the "spectrum" of domain sizes which can exist and the properties of the solid which are related to the elements of this "spectrum" singly and in combinations.

Evidence for Structural Domains in Filaments

Macroscopic Evidence for the Existence of Domains in Filaments

The earliest suggestion that the mechanical strength of filaments may be associated with a characteristic length element appears to have been made by Peirce in 1926 [27]. He used the term "weakest link" to refer to a particular domain of such dimensions and micro construction that as a macroscopically applied load is monotonically increased, rupture will occur within this domain at a lower total acting load than in any other. The load at which a particular specimen breaks is then simply determined by the largest load supportable by the weakest domain present in any particular specimen. The variation in rupture load observed from specimen to specimen can be related simply to the frequency distribution of the possible domain strengths. These ideas are expressible in mathematical form if one assumes that the size variations among the domains are unimportant and can be approximated by some "mean" value (Peirce tacitly assumed this in his work, but made no special point of it). The size of the specimen is then simply proportional to the total number of such "average" domains existing in the specimen. One could observe the form of the distribution of the strengths of these average domains if he could experimentally obtain specimens containing only one mean domain. It would be a frequency plot of the results of many repetitions of the rupture-load determination using specimens composed of single domains. Unfortunately, there is no simple way of directly determining the necessary specimen dimensions. Hence, one is forced to vary systematically the specimen size and study the rupture-load distribution as a function of specimen size. These studies have been termed "size-effect studies." The distributions of the rupture-load values expressed as probabilities can be related mathematically to the macroscopic dimensions of the specimen, and the distribution of

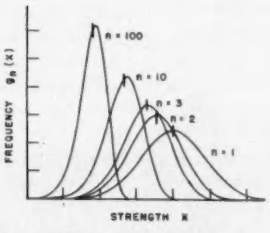

FIG. 1. *Normalized strength distributions (after Peirce [27]). Strength is measured in arbitrary units from the mean-domain strength. Distribution of single-domain strength* (n = 1) *is assumed to be Gaussian. The mean of the distribution for various-sized specimens* (n = 2, 3, 10, 100) *is indicated by a vertical line in each case.*

* The term "microscopic" is not used to imply distances resolvable by the light microscope, but rather to imply length elements characteristic of interatomic spacings, including spacing between domains.

strengths associated with the average domain size. If one assumes that the number of these average domains present in long thin fibers and filaments can be characterized by a measure of the length of the specimen, the probability, $g_n(x)$, of observing a specimen of length n breaking between a load of x and $x + dx$ is related to the distribution of strengths of the elemental average domain, $f(x)$, by [11]

$$g_n(x) = nf(x)\left[1 - \int_0^x f(x)dx\right]^{n-1}. \qquad (1)$$

Under the assumptions given above, one can attempt to obtain $f(x)$ from observations of $g_n(x)$ by using equation (1).

The distribution function $f(x)$ expresses the probability that any given average domain will have a strength lying between x and $x + dx$. The mathematical forms of this function have not been determined to date for particular cases, but are probably relatively unimportant in determining the qualitative features of the observed distribution functions $g_n(x)$ as n is varied. In Figure 1 are shown plots of $g_n(x)$, assuming $f(x)$ to be Gaussian in character [27]. As n increases—*i.e.*, as the specimen size increases—the $g_n(x)$ distribution curve becomes narrower and has a higher peak; further, the mean values of $g_n(x)$, which are indicated by the vertical lines, move progressively to lower x values. In general, it would be expected that physically reasonable $f(x)$ functions would yield essentially similar curves, but this requires additional investigation. In fact, the physical existence of such a function $f(x)$ is by no means certain. The conditions for atomic and molecular cooperation which would lead to such a function have yet to be determined.

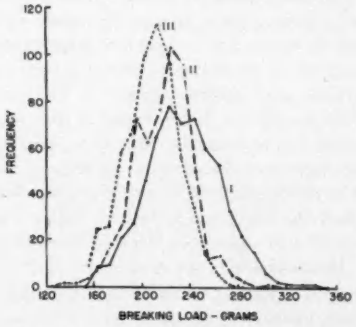

FIG. 2. *Experimental distribution functions* $g_n(x)$ vs. x *for cotton yarns (after Peirce [27]).*

It is interesting to note the experimental form of $g_n(x)$. Figure 2 shows curves obtained by Peirce [27] using cotton yarn specimens of various lengths. Figure 3 shows similar distributions obtained by George and LaTorre [13] using continuous-filament nylon yarns and A.S.T.M. testing procedures for the inclined-plane type of loading device.

Without going into details of the mathematical theory of the analysis, it may be stated that the cumulative distribution functions $G_n(x)$ of the observed probability distribution $g_n(x)$ are given as the integrals

$$G_n(x) \equiv \int_0^x g_n(x)dx. \qquad (2)$$

For two specimens, sizes m and n are related by [13]

$$\frac{m}{n} = \frac{\ln[1 - G_n(x)]}{\ln[1 - G_m(x)]}. \qquad (3)$$

This ratio is easily calculated and plotted from experimental data as a function of x. The ratio may be expressed as a function of the observed quantities only. If $f(x)$ exists, we will expect, then, that the ratio m/n will be found experimentally as a constant independent of x. Using the nylon distributions shown previously, this ratio has been computed, and a plot of the data is shown in Figure 4. This is obviously not the result predicted by simple one-dimensional theory. Comparisons of the distribution of the cotton yarns shown in Figure 2 yield similar ambiguities.

The nylon yarns studied had very low twist, about 1 turn per inch. In a specimen 3 in. long,

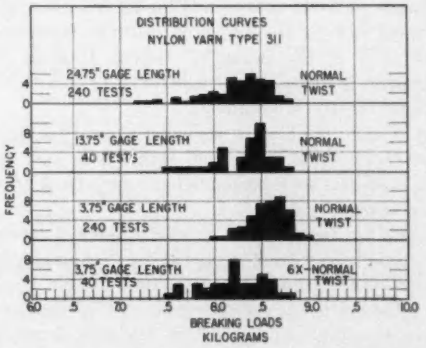

FIG. 3. *Experimental distribution functions* $g_n(x)$ vs. x *for continuous-filament nylon yarn (Type 311) (after George and LaTorre [13]).*

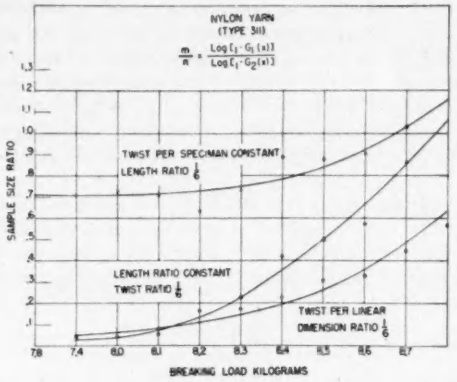

FIG. 4. *Sample-size ratio* m/n vs. *strength as computed from cumulative distribution functions* $G_i(x)$, i = m,n, *using equation (3); Nylon Type 311 yarn (5/210/34) (after George and LaTorre [13]).*

the yarn has a total twist of 6 π radians, while a specimen 9 in. long has a total twist of 18 π radians. The size effect could be measured effectively if a specimen with constant total twist were used, varying only the pitch of the twist angle as the length is changed. This experiment is easily done, and the plot of the ratio of cumulative distributions observed for a total twist of 18 π radians, varying the length by a factor of 6 to 1, is shown in Figure 4. Possibly our simple concepts can be maintained if the yarn twist is handled properly—*i.e.*, by keeping the total twist angle constant in making the linear size-effect study. Presumably the effects in yarns of balanced constructions and higher twist are more complex than in the low-twist continuous-filament yarn used in the example. Figure 3 shows the alteration in distribution functions $g_n(x)$ with the variation in the twist angle.

It is seen, then, that the experimental curves of $g_n(x)$ obtained on yarn yield rather wide distributions and that such parameters as yarn twist affect the results.

Some apparently very careful size-effect studies on rayon yarns were reported by Bellinson [1]. Selections from his data are given in Table I. In the table are listed the specimen size, n, the mean strength, and probable average deviation from the mean. Also given are similar data of Squires and Ruark [33] obtained at constant rates of loading using copper wire of high purity and uniformity.

TABLE I. FILAMENT SIZE EFFECTS

Rayon yarn (150/42)
(After Bellinson [1])

No. of specimens	Length (in.)	Strength (g.)	Deviation (g.)	Deviation (%)
48	5.00	274.32	4.45	1.6
48	9.97	271.02	2.94	1.1
44	14.97	270.77	3.72	1.3
48	19.96	271.49	4.07	1.5

Copper (OF) 24 B&S wire
(After Squires and Ruark [33])

No. of specimens	Length (in.)	Strength (g.)	Deviation (g.)	Deviation (%)
200	6.00	4777.3	17.5	0.37
—	12.00	4771.5	—	—
—	48.00	4767.5	—	—
—	1200.00	4724.0	—	—

Copper (OF)
(After Anaconda Copper Company)

Gage B&S	Strength (p.s.i.)	Deviation (%)
16	33,200	1.4
10	36,140	1.2

The striking results of these data are: (1) the smallness of the probable error regardless of sample size, n, which is indicative of the width of the distribution; and (2) the smallness of the size effect—that is, the smallness in the variation of the mean rupture stress with sample size. These conclusions are quite different from those for the nylon yarn samples discussed above. This difference is not too surprising in view of the complexity of the yarn, the difficulty of obtaining uniform load distributions, etc. It would appear, then, that such widely different materials as rayon and copper are both capable of possessing quite small size effects and very narrow distributions of rupture strength. The physical interpretation of the narrowness of the strength distribution curve must be that *if* an average domain characterizes the strength of these materials, it must be quite small, or, in other words, the number within the specimen is large. Unfortunately, the form of $f(x)$ cannot be derived from the work cited. In its absence, we are unable to "fit" the data in such a way as to show that domains exist, or obtain estimates of their size. Fortunately, such data can be obtained from micro experiments involving x-ray diffraction.

Microscopic Evidence for the Existence of Strength-Determining Domains in Filaments

The diffraction of x-rays by real solids provides the most conclusive microscopic evidence obtained to date for the existence of domains which can be related to the mechanical strength of solids.

The ideal solid, composed of the regular repetition of a certain elementary atomic configuration, will diffract a collimated beam of monochromatic x-rays in accordance with Bragg's law:

$$n\lambda = 2a \sin \theta \tag{4}$$

(the use of n in this connection will cause no ambiguity). A more detailed analysis shows that the diffraction of a narrow pencil of monochromatic radiation is accompanied by a slight increase in the cross-sectional dimensions of the diffracted pencil. Experiments on real solids consistently show a much greater enlargement in the dimensions of the diffracted beam than predicted by theory for an ideal crystal [14]. This enlargement in the diffracted pencil is termed "broadening." Further, the intensity of the radiation within the diffracted pencil is experimentally greater than calculated from the theory of such an ideal lattice. These departures from theory are interpreted in terms of the imperfection of the real solid—that is, in terms of its departure from the ideal lattice.

There are two types of imperfection broadening which have been used to discuss theoretically the radial enlargement of a diffracted pencil of x-rays. One is termed "strain broadening" and the other "particle broadening."

Strain broadening [4] is thought of as being the result of a shift, $\Delta\theta_s$, in the Bragg angle, θ, accompanying a local average change in lattice parameter a to $a + \Delta a$, and is calculated from Bragg's law by differentiation:

$$\Delta\theta_s = -\frac{\Delta a}{a} \tan \theta. \tag{5}$$

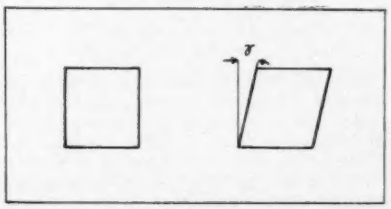

FIG. 5. *Simple domain (after Bragg [3]).*

Particle broadening, $\Delta\theta_p$, is obtained from a relation first given by Scherrer [30] which is essentially the formula for the width of a spectral line diffracted by a grating of N spaces along the grating,

$$\Delta\theta_p = \frac{K}{L} \frac{\lambda}{\cos \theta}, \tag{6}$$

where L is the particle dimension, and K a dimensionless constant of the order of unity. The formula given for the strain broadening has the same dependence on λ and θ as the particle-broadening relation, which can be seen by substituting Bragg's law into equation (5):

$$\Delta\theta_s = -\frac{\Delta a}{2a^2} n \frac{\lambda}{\cos \theta}. \tag{7}$$

The coefficient $\Delta a/2a^2$ has the dimensions of a reciprocal length, and is completely determined by $\Delta\theta$, λ, and θ. It is thus seen that, regardless of interpretation preferred, the broadness measure coupled with λ and θ yields a measure of a length quantity. The existence of broadening too large to be explained by the geometry of the experimental arrangement is evidence, then, for the existence of the length measure L which, we assert, constitutes a domain dimension or is a function of various characteristic domain dimensions. For the present discussion we shall confine our attention to the simpler view that the characteristic length, L, computed from x-ray broadness data characterizes the domain dimension. We shall now attempt to relate this quantity to the strength of the solid.

The changes in broadness values seem to saturate with increasing plastic strain. Hence, it would seem natural to relate the ultimate strength with the value of L derived from materials which have been subjected to large plastic strains.

A simple microscopic model for the dependence of mechanical strength on the domain dimension L characterized by the x-ray broadening data has been given by Bragg [3, 4]. He considered the domain to be square in two dimensions, as sketched in Figure 5. The imposition of macroscopic loads or deformations results in the development of a certain shear in the domain. Let a measure the lattice parameter in the direction of the shear which constitutes the *element* of plastic motion within the domain. Bragg showed, for angles of shear $\gamma > a/L$, that the shear-strain energy was greater within the domain than it would be if some plane parallel to the edge were to undergo a crystal-

lographic slip of amount a. He was able to show that for $\gamma < a/L$ slip would lead to increased shear-strain energy storage within the domain. Hence, shear angles of the order $\gamma \sim a/L$ would be expected to lead to a general breakdown of the solid by plastic flow. The macroscopic stress at which this would occur would be given by

$$\sigma \sim \frac{a}{L} G, \tag{8}$$

where G represents the shear modulus for the domain.

In general, it is not possible to obtain with certainty the precise value of G to be used in testing the relation developed above, but for order-of-magnitude comparisons the bulk shear modulus should prove adequate. In Table II are listed values of strength obtained from x-ray broadness data and from the above relation for a variety of solids, metallic and nonmetallic [2, 4, 10, 24]. The agreement is, on the whole, very satisfactory, giving confidence that the general approach outlined above is capable of unifying experience.

Thus, the existence has been demonstrated of domains which can be related to the ultimate strength of the solid. It has also been shown that these domains are sufficiently small to account for the width of the distributions of rupture strengths observed in the wire and yarn size-effect experiments cited.

TABLE II

(After Wood and Rachinger [35])

Material	Domain (Å)	Parameter (Å)	Modulus (10^3 tons/in.^{2})	Strength (tons/in.^{2}) Calculated	Observed
Iron	300	2.48	3.9	32	30
Molybdenum	420	2.72	8.6	56	75
Tantalum	240	2.85	4.0	47	58
Tungsten	290	2.74	10.0	95	110

(After Bergmann, Fankuchen, and Mark [2])

			(p.s.i.)	(p.s.i.)	
Nylon	140	2.5	6×10^8	1.1×10^4	1.2×10^4

(After Mark [24])

			(dynes/cm.^{2})	(dynes/cm.^{2})	
Ramie (dry)	600	6	5.2×10^{11}	5.2×10^9	
	600	10	5.2×10^{11}	8.6×10^9	3.0×10^9
Ramie (wet)	600	6	1.9×10^{11}	1.9×10^9	
	600	10	1.9×10^{11}	3.1×10^9	9×10^9

(After Mark [24] (theoretical))

"Slippage" theory	$9. \times 10^9$
End-bond rupture theory	2.7×10^9
Primary-bond rupture theory	7.2×10^{10}

Conceptions of the Microscopic Domains in Solids

The agreement obtained between x-ray broadness data and strength measures naturally raises interest as to the more precise nature of the microscopic details of domain interlocking and the crystallographic arrangements within the boundary regions. Such pictures are possible theoretically for lattcies of simple cubic symmetry in two dimensions. They are constructed from the elementary units of disorder called "dislocations." The two-dimensional picture of Taylor [31, 34] dislocations is shown in Figure 6. These may be obtained by removing one-half of the atoms in a certain plane segment normal to the figure (between + and − in Figure 6), and allowing the surrounding atoms to fill in the void thus created. An alternate view is that the dislocation shown here constitutes the result of partial insertions of two extra atom rows [29]. Now suppose that we have two regions of perfect order which we wish to fit together with arrays of this elemental disorder. Burgers [5, 6] pictured the situation for two cases, one where the orientation difference between the domains is relatively small and one where it is large. When the orientation difference is large, he fitted the two regions together as shown in Figure 7.

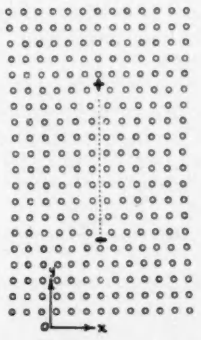

FIG. 6. *Lattice region (supposed to extend to infinity in the direction of the z-axis, perpendicular to the plane of the drawing) with two edge-type dislocations (Taylor dislocations), one positive (above) and one negative (below). The dislocations are obtained by removing the atoms over a certain area of the lattice perpendicular to the x-axis. The dislocation lines extend at + and − parallel to the z-axis (after Burgers [5, 7]).*

A similar arrangement, applicable for smaller orientation differences, is shown in Figure 8, which might also be taken for the case when the crystals are composed of long molecules instead of atoms. The arrangement in Figure 9 is a conceptual arrangement of the crystallites in a metal, where the angular differences between domain directions are large [5, 7]. Figure 10 shows an arrangement suggested by Meredith [26] for junctions between the crystallites in cellulose. There is a striking similarity between the domains in this diagram and the arrangement for metals shown in Figure 8.

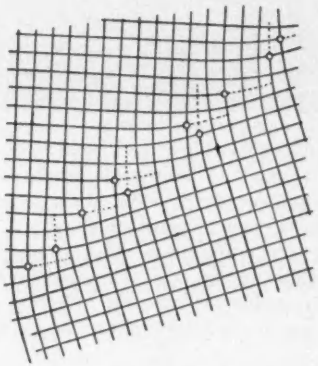

FIG. 7. *Schematic picture of a transition layer ("grain boundary") between two lattice blocks, including a large angle. The layer is built up of* two *sets of dislocation lines of the edge type (after Burgers [5, 7]).*

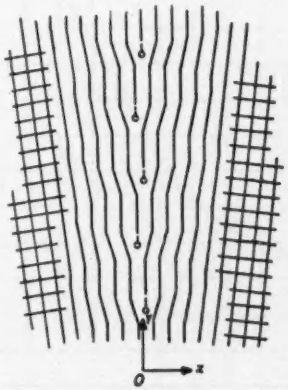

FIG. 8. *Schematic picture of a transition surface between two lattice domains, formed by a set of parallel dislocation lines of edge type, all situated in the plane* x = 0. *(after Burgers [5,7]).*

Strength Experiments Viewed in Terms of Domain Dynamics

General

Up to the present we have considered strength in terms of the load required to produce rupture. The term "strength" infers a load to produce an arbitrary macroscopic deformation. In general, three of the four macroscopic variables which each stress-strain relation implies can be controlled. The variables are: (1) load, (2) deformation, (3) thermal environment, and (4) chemical environment. Each may be a function of time. Usually, the last two variables are kept constant, and the time control of one of the other two is varied. Thus, load control results in constant load creep,

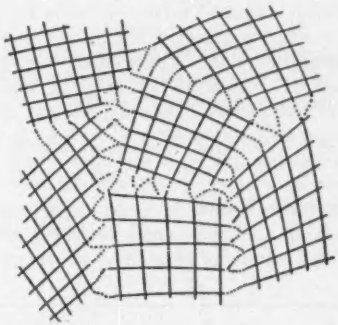

FIG. 9. *Schematic representation of the cold-worked state: elastically stressed and bent "mosaic-blocks" connected by transition layers of dislocated atoms.*

FIG. 10. *Oriented cellulose (after Meredith [26].) Compare with Figure 8.*

constant stress creep, constant rate of load, and constant rate of stress tests. The resulting deformations are then studied as a function of time. The other class of experiments, deformation control, includes constant strain or stress relaxation and constant strain rate tests. Discussed below are selected examples from these simpler forms of macroscopic study which suggest the utility of the domain concept in aiding in the microscopic understanding of the experiments.

Load-Induced Domain-Motions

The first example is the familiar constant rate of load application test. In Figure 11 (left) is shown a typical load-extension diagram for such a test on an oriented Type 200 Nylon bundle. The stress-strain curve (right) was obtained from a single crystal of high-purity aluminum, where again the rate of load application was held constant. The shapes of these two curves are remarkably similar.

Now let us consider the changes in the broadening of x-ray fiber patterns which accompanies the straining of the nylon. These effects were recently measured by Kauffman [17, 18] at the Naval Research Laboratory. The experiment involved the abrupt termination of the loading cycle at a time t corresponding to a given extension. This was done by placing a stop on the track of an ordinary inclined-plane type of yarn tester. A special clamp was made which allowed transfer of a portion of a bundle of fibers under constant strain from the testing machine to an ordinary diffraction unit. This transfer time and exposure time together were something less than 2½ hrs. on the average. The fiber patterns (see Figure 12 for a typical example) were obtained on film in the usual way, and were analyzed by making photometer traces (1) along the radius vector, the central beam being chosen as origin, and (2) at right angles to the radius. The widths of the most prominent fiber spot from these traces, measured at half-maximum intensity in radians from an origin in the specimen, constituted the broadness measure used. The radial broadness, as discussed earlier, measures essentially the increase of the domain size; the angular broadness measures the distribution of orientations, perfect fibering yielding very small angular broadness and completely random orientation yielding the Debye-Scherrer ring. Figures 13 and 14 show the results obtained. These data show clearly some of the dynamic behavior of the strength-sensitive domains in the case of nylon. Once the plastic state is fully achieved and the strain is, say, 1%, the radial broadness is essentially unchanged until the inflection point of the load-strain curve is reached (at a strain of

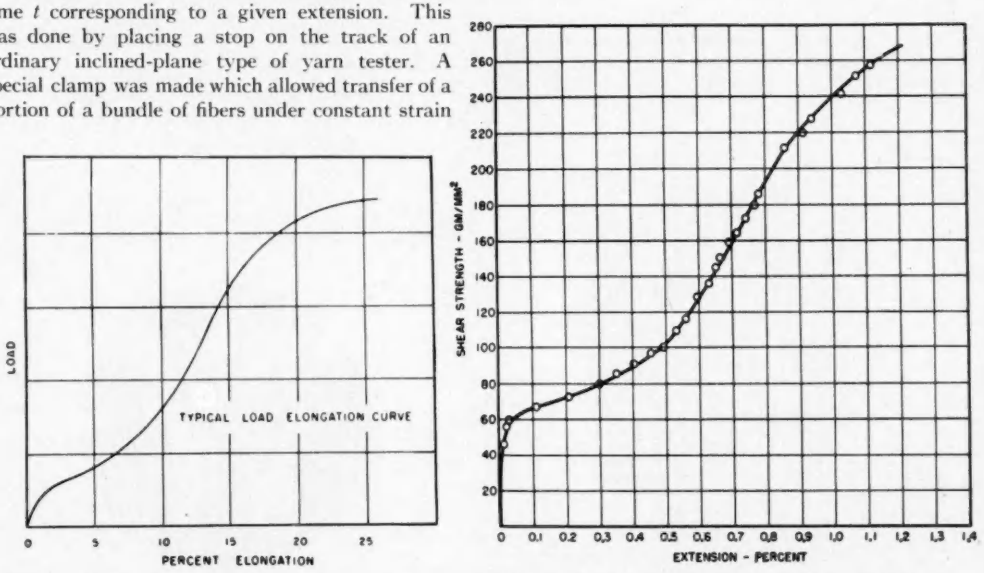

FIG. 11. Left—*Typical load-elongation curve for Type 200 Nylon (after Kauffman and George [18]).* Right—*Resolved stress-strain relation for a single crystal of high-purity aluminum (after Miller and Milligan [37]).*

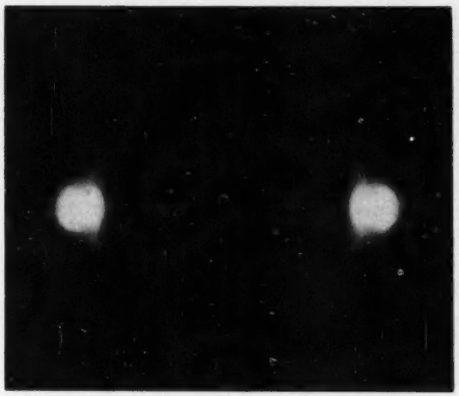

FIG. 12. *Typical diffraction pattern obtained from Type 200 Nylon fiber bundle (Cu, $K_{\alpha 1}$ radiation).*

about 14% in this case). The fact that most of the change observed in the radial broadness is confined to strains greater than the inflectional strain suggests that the average domain spacing or dimension is essentially unaltered during the early portion of the strain epoch. In interpretation, after the inflection in the load-strain curve is reached the domains decrease in size, since the broadness increases at an ever slower rate and has some appearance of saturating at about the rupture strain. It is this saturating value of broadness which is compared with rupture strength. Note the changes in the angular broadness shown in Figure 13. Initially, this decreases, suggesting a rotation of the domains toward the fiber axis. At the inflection point of the load-strain curve this rotation process sharply reverses; hence, as the domains split up into smaller regions the fiber structure becomes less perfect.

There is evidence in the literature that the domains of many metallic solids behave in a somewhat similar manner, but it is less direct and much less complete than that shown for nylon [9, 19]. It would appear that the time-dependence of the domain reactions to applied loads may control the subsequent macroscopic strain changes.

The time-dependence of the domain motions in a controlled-loading experiment is not directly under the control of the investigator. The macroscopic strain resulting from a given load application is chosen by the material in a fashion which is the object of the present study. A greater demand on the domain reactions is made if one attempts to control the macroscopic strain imposed on the specimen and to observe the macroscopic loads resisting the imposed deformations. This allows inference of the domain dynamics on a micro scale.

Domain Dynamics Inferred from Controlled Macroscopic Rates of True Straining

The true strain rate, $\dot{\epsilon}$, is defined [23] for a fiber of initial length l_0 by

$$\dot{\epsilon} = \frac{1}{l}\frac{dl}{dt},$$

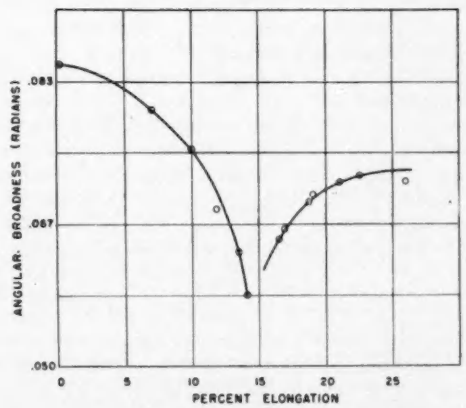

FIG. 13. *Angular broadness* vs. *tensile elongation, Type 200 Nylon (after Kauffman and George [18]).*

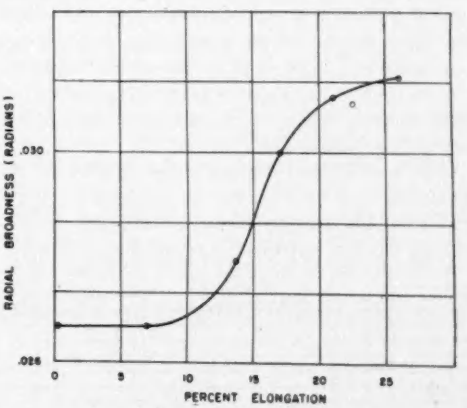

FIG. 14. *Radial broadness* vs. *tensile elongation, Type 200 Nylon (after Kauffman and George [18]).*

where l refers to the length of the fiber at time t. If this definition of strain rate is used and if the strain is macroscopically homogeneous, a constant true strain rate implies that the change of length per unit length per unit time is constant throughout the fiber. This is not the case when the usual engineering definition of strain rate, $\dot{\epsilon}_1$, is used,

$$\dot{\epsilon}_1 = \frac{V}{l_0},$$

where V is the velocity of the moving head of the testing machine and l_0 is the initial gage length. The two definitions are equivalent only at $t = 0$, the engineering strain rate tending to smaller values as the strain is increased.

LaTorre [20], working at the Naval Research Laboratory, has perfected mechanical devices which accurately control the true strain rate. Figure 15 shows a schematic diagram of a simple model. The cam is so shaped that the monofilament specimen is caused to change length approximately as given by the equation

$$l = l_0 \exp(kt),$$

where k is the true strain rate desired. By changing the speed of angular rotation of the cam, various values of k can be obtained between about 10^{-7} and 10^{-1} sec.$^{-1}$. The loads resisting the imposed deformations can be measured as functions of the time by recording the deflection of a sensitive double cantilever spring. The deflection is picked up by a linear differential transformer, the output of which is plotted on a recording photoelectric potentiometer. (A typical record is shown in Figure 16.) The typical specimen (approximately 10μ diameter fiber) is mounted in heads as described previously [21].

Stress and strain are easily computed from the recorded load-time curve by assuming that the volume of the specimen remains essentially constant during the homogeneous portion of the deformation. These relations are:

$$\sigma = \frac{\mathfrak{L}}{A} = \frac{\mathfrak{L}}{A}\exp(kt)$$

$$\epsilon = \ln \frac{l}{l_0} = kt,$$

where $\mathfrak{L}$ is the load.

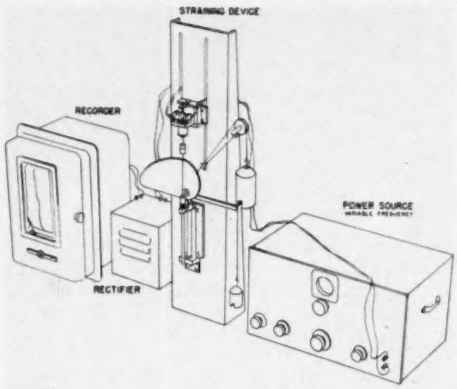

FIG. 15. *Schematic arrangement for constant true tensile strain rate tests of single fibers (after LaTorre and George [20]).*

The effects of varying k, the true strain rate, are shown in Figures 17 and 18, which show values of stress and load *vs.* time for nylon [21] and cadmium single filaments [22], respectively, at room temperature. The end-points of such stress-strain or load-time records yield values of the rupture load as a function of strain rate. These strain-rate effects on ultimate strength are shown in Figures 19 and 20. Figure 19 shows the effects for cadmium of high purity, Figure 20 for nylon. The curves are similar and suggest during the slower strain rates that the domains are growing during the test time. Such growth processes in metals are termed "recovery" [7]. It would appear, then, that in the nylon a type of "recovery" can occur which may be analogous to the phenomenon in metals.

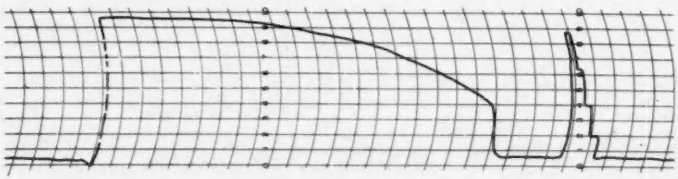

FIG. 16. *Typical load-elongation record of single fiber constant true strain rate test (.001 in. Cu wire). Load is the curvilinear ordinate; time is measured from right to left.*

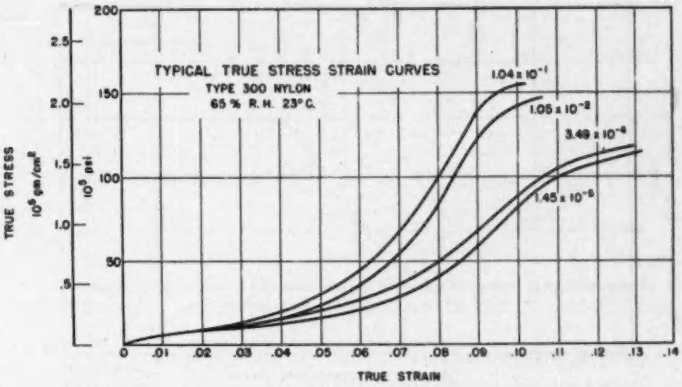

FIG. 17. *Typical true stress-strain curves for nylon monofilaments, pulled at constant true strain rates. Parameters on the curves represent true strain rate in sec.$^{-1}$ (after LaTorre and George [20]).*

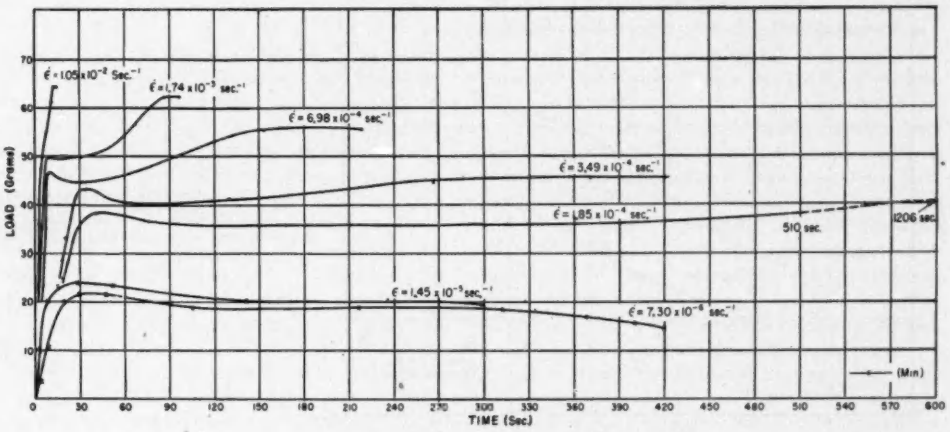
ε̇ = 1.05 x 10⁻² Sec.⁻¹
ε̇ = 1.74 x 10⁻³ sec.⁻¹
ε̇ = 6.98 x 10⁻⁴ sec.⁻¹
ε̇ = 3.49 x 10⁻⁴ sec.⁻¹
ε̇ = 1.85 x 10⁻⁴ sec.⁻¹
510 sec.
1206 sec.
ε̇ = 1.45 x 10⁻⁵ sec.⁻¹
ε̇ = 7.30 x 10⁻⁶ sec.⁻¹
LOAD (Grams)
(Min)
TIME (Sec)

FIG. 18. *Load-time curves for cadmium wire, pulled at constant true strain rates (after LaTorre and George [22]).*

As the strain rate is increased to near unity, apparently the process of recovery is not operative. These curves suggest that recovery is a time-sensitive phenomenon, as in fact we know it to be from other arguments. It would appear that through the use of a constant true strain rate deformation technique, a strong dependence of strength on time can be exhibited which is an important experimental aspect of plastic flowing.

If the concept of domain control of strength is at least partially correct, one would expect the disordered regions surrounding them to be relatively unstable regions of high free energy. Thus, it would be reasonable to expect for certain strain rates that these relatively unstable regions would seek lower energy states. Diffusion processes would provide adequate mechanisms for the transitions. One would expect that any alteration of diffusion mechanisms would lead to changes in the strength. Those effects which effectively slow down diffusion would lead to increases in strength, and vice versa. The faster test results, where diffusion is surely less important, are in agreement with these speculations. It is well known that the relative humidity at which a textile fiber is conditioned is related in some way to the ultimate strength of the fiber. It is of interest to see if the results of certain preliminary humidity experiments

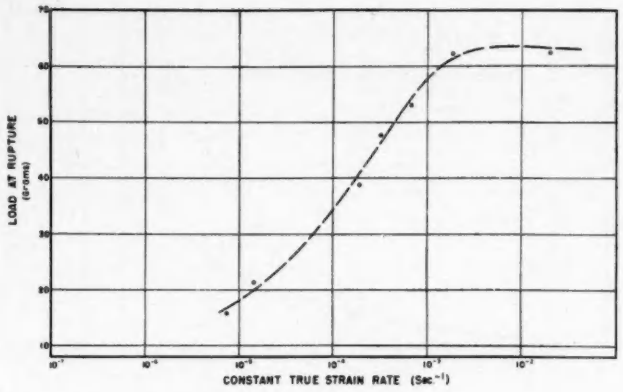

FIG. 19. *Strength* vs. *true strain rate for cadmium wire.*

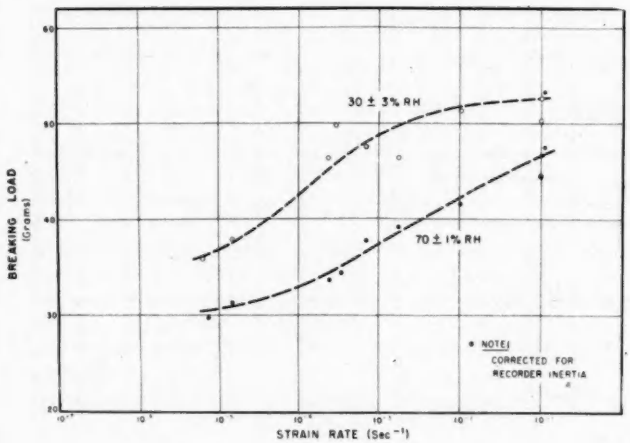

FIG. 20. *Strength* vs. *true strain rate for Type 300 Nylon monofilaments tested at two environmental humidities (after LaTorre [20]).*

using constant strain rates are qualitatively compatible with the idea of domain control of strength properties.

Humidity-Strength Effects Viewed as a Consequence of H_2O-Domain Interactions

One of the more reproducible qualitative effects of relative humidity on mechanical properties is obtained for the case of single fibers of ramie. These were first obtained at constant velocities of extension using the apparatus of Polanyi [28] by Karger and Schmid [16] in 1925. The effects are: (1) increased rupture strength with increased H_2O absorbed within and perhaps on the surface of the fiber; and (2) increased plasticity at low stress levels with increased humidity. The data obtained using the constant rate of extension are shown in Figure 21. Using single ramie fibers and the constant true strain rate deformation equipment described earlier, similar curves were obtained at 50% and 70% R.H. and in the wet state [25]. These are shown in Figure 22. Both sets of data show the same qualitative effects, but quantitatively the constant strain rate data give larger effects. One cannot be sure whether this is due to the strain rate control or to the degumming process used for these samples of ramie. The ramie used in our laboratory by Mr. McLean was representative of recent American and Swiss degumming practice, whereas the earlier work was on older European stock. We

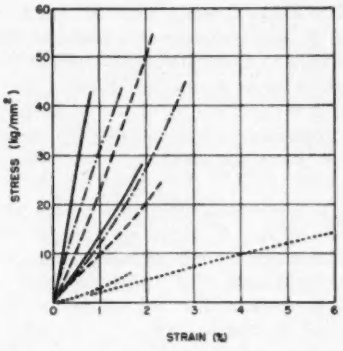

FIG. 21. *Stress* vs. *elongation, ramie monofilaments at various environmental humidities (high to low humidities are from left to right) (after Karger and Schmid [16]).*

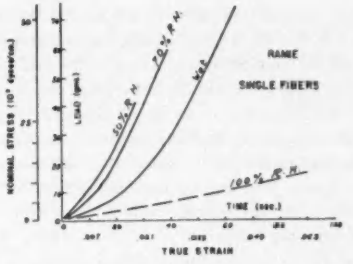

FIG. 22. *Stress* vs. *elongation, ramie single filaments strained at constant true strain rates (after McLean [25]).*

have made a few preliminary tests on Swiss ramie using the constant strain rate device, and find little difference from the American ramie, especially in breaking strength. Figure 23 shows a plot of some of our breaking-strength data as a function of relative humidity. The number of tests is quite small, approximately 20 per point, but the trend is clear. Extrapolating to zero R.H., these data show that H_2O at 100% R.H. strengthens the fibers used by between 300% and 400% of the dry value.

The interpretation of this H_2O strengthening effect in cellulose has not received much attention in the literature; however, the increased low-stress-level plasticity was recently discussed by Hermanne [15] in terms of micro Brownian motions of chain segments in the intercrystallite or so-called "amorphous" regions. The strengthening action is not too difficult to explain within the domain picture, while in no way requiring modification of the picture presented by Hermanne for the plasticizing effect. The interdomain material is highly disordered. It is precisely this region of high free energy in which the wandering H_2O molecule prefers to concentrate, since this intrusion will be accomplished with proportionately less change in free energy than within a domain where high order persists with low free energy. The intrusion of the H_2O locally reduces the van der Waals' attraction between the disordered molecules, thereby increasing the potential deformation of these regions by entropy mechanisms. As the strain increases, surely some additional crystallization and orientation of the ordered domains occurs since the load-strain relation appears to approach the inflection region. The presence of certain amounts of H_2O will impede this domain growth, the higher conditioning humidities

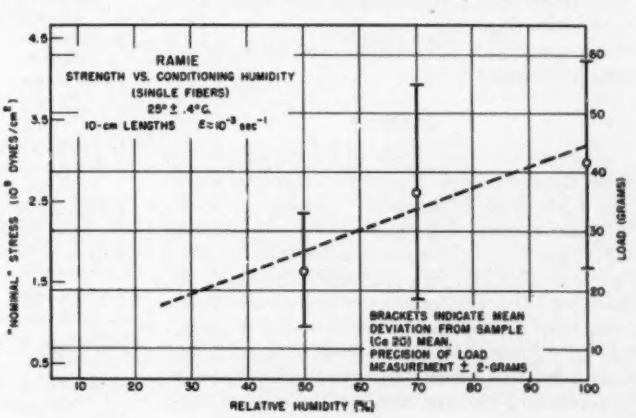
RAMIE
STRENGTH VS. CONDITIONING HUMIDITY
(SINGLE FIBERS)
25° ± .4°C.
10-cm LENGTHS
BRACKETS INDICATE MEAN DEVIATION FROM SAMPLE (Ca 20) MEAN. PRECISION OF LOAD MEASUREMENT ± 2-GRAMS
"NOMINAL" STRESS (10⁹ DYNES/cm²)
LOAD (GRAMS)
RELATIVE HUMIDITY (%)

FIG. 23. *Breaking strength* vs. *relative humidity of the test environment, ramie monofilaments (after McLean [25]).*

tending, on the average, to smaller domains and, consequently, to higher strengths in terms of the assumed relation between domain size and ultimate strength. In addition to impeding the growth of the crystallite, the presence of the H_2O molecules may, at sufficiently high stress levels, harden up the disordered region by causing the development of locally lower free-energy regions immediately surrounding the intruding molecules. The macroscopic stresses required to move these regions, leading to a macroscopic strain change, will be higher the higher the concentration of H_2O and its attendant local reduction in free energy, which essentially increases the activation potential for the straining process. The recovery of many "delayed deformations" which are locked in by dryer deformations is in no way altered by this hardening effect, which is qualitatively quite similar to a recent explanation by Cottrell [8] of the action of carbon atoms in blocking disorder in the iron lattice by reducing the free energy of a dislocation upon intrusion into that disorder.

The large difference observed between the constant true strain rate test and constant velocity of extension tests of ramie can be used to infer one further interesting time effect—namely, the possible existence of some region of strain rate where the strength properties of cellulose vary sharply with straining speed, perhaps more sharply than for either cadmium or nylon. The data of Schmid [16] was for an average strain rate of about one-tenth that used for the Naval Research Laboratory true strain rate study. Between these two strain rates, the variation of stress at given strain appears to increase by a factor of between 3 or 4, which is a very sharp strain rate dependence. A rise of this magnitude occurs in cadmium in about three decades in straining speed.

Summary

Evidence has been presented for the existence of small domains of size intermediate between atomic and macroscopic dimensions. A study of the distribution of strength data allows the inference that the domains are quite numerous, but does not allow their size to be fixed as to order of magnitude. On the other hand, studies of x-ray line broadness as a function of plastic strain allow the order of magnitude of the dimensions to be fixed. These dimensions seem to correlate with strength properties. By considering the crystallographic transitions from domain to domain, one arrives at conceptual pictures of the fine structure of a solid on this intermediate scale. Examples of this concept in metals and plastics were presented. Finally, the effects of varying the relative humidity on fiber strength properties were discussed, and the experimental results were found to be consistent with the domain concepts.

Certain new experimental procedures and data were presented. A constant true strain rate fiber deformation mechanism was discussed. The data obtained with this device suggest that the changes in domain size are related to diffusion effects, and that these changes can be impeded by absorbed H_2O molecules in the case of cellulose.

It is hoped that this discussion is suggestive of *an approach* to filament-strength problems. The thesis presented is speculative at many points, and the data used in its support are far from overwhelming in other categories. In spite of these very valid criticisms, the viewpoints do seem capable of dealing with a variety of the somewhat complex and incompletely understood mechanical properties of filamentous solids.

Literature Cited

1. Bellinson, H. R., TEXTILE RESEARCH **10**, 287 (1940).
2. Bergmann, M. E., Fankuchen, I., and Mark, H., TEXTILE RESEARCH JOURNAL **18**, 1 (1948).
3. Bragg, L., *Nature* **151**, 585 (1943).
4. Bragg, L., *Proc. Cambridge Phil. Soc.* **45**, No. 1, 125–30 (1949).
5. Burgers, J. M., *Proc. Koninkl. Akad. Wetenschap. Amsterdam* **42**, 293, 315, 378 (1939).
6. Burgers, J. M., *Proc. Phys. Soc.* **52**, 23 (1940).
7. Burgers, W. G., *Proc. Koninkl. Akad. Wetenschap. Amsterdam* **50**, 452, 719, 857 (1947).
8. Cottrell, A. H., in "Bristol Conf. on Strength of Solids," Phys. Soc. London, 1948, pp. 30–8.
9. Dehlinger, U., and Kochendorfer, A., *Z. Krist.* **101**, 134 (1939).
10. Duwez, P., *Phys. Rev.* **47**, 494 (1935).
11. Epstein, B., *J. Applied Phys.* **19**, 140, 147 (1948).
12. Freudenthal, A. M., and Reiner, M., *J. Applied Mechanics*, Paper APM-6 (1948).
13. George, W., and LaTorre, R., *Phys. Rev.* **74**, 1256 (A) (1948).
14. Guinier, A., *Proc. Roy. Soc.* (*London*) **52**, 310, 324 (1945).
15. Hermanne, L., TEXTILE RESEARCH JOURNAL **19**, 61–72 (1949).
16. Karger, I., and Schmid, E., *Z. tech. Physik* **6**, 124 (1925).
17. Kauffman, J., Thesis, Physics Dept., Univ. of Maryland, June 1949.

18. Kauffman, J., and George, W., *J. Applied Phys.* **21**, 431 (1950).
19. Koehler, J. S., and Blewitt, T. H., *Phys. Rev.* **75**, 1952–3 (L) (1949).
20. LaTorre, R., and George, W., *Phys. Rev.* **75**, 1309 (A) (1949).
21. LaTorre, R., and George, W., TEXTILE RESEARCH JOURNAL **19**, 830 (1949).
22. LaTorre, R., and George, W., *Bull. Am. Phys. Soc.* **24**, No. 5, 27 (1949)
23. Ludwick, P., "Elemente der Technologischen Mechanik," Berlin, 1909.
24. Mark, H., in "Cellulose and Its Derivatives" (E. Ott, editor), New York, Interscience, p. 990 *et seq.*
25. McLean, E., and George, W., unpublished.
26. Meredith, R., *J. Textile Inst.* **37**, 469–80 (1946).
27. Peirce, F. T., *J. Textile Inst.* **17**, T355 (1926).
28. Polanyi, M., *Z. tech. Physik* **6**, 121 (1925).
29. Polanyi, M., *Z. Physik* **89**, 660 (1934).
30. Scherrer, P., "Nach. Gesell. Wiss.," Göttingen, Zitsgungsber, 1918 (through Zsigmondy, R., "Kolloidchemie," Leipzig, Spamer, 1920).
31. Sietz, F., and Reed, T. A., *J. Applied Phys.* **12**, 100, 120, 538 (1941).
32. Smekal, A., *Naturw.* **15**, 106–88 (1936).
33. Squires, R. M., and Ruark, A. E., *Phys. Rev.* **65**, 365 (A) (1944).
34. Taylor, G. I., *Proc. Roy. Soc.* (*London*) **A195**, 362 (1934); Orowan, E., *Z. Phys.* **89**, 634 (1934).
35. Wood, W. A., and Rachinger, W. A., *J. Inst. Metals* **75**, 571–94 (1949).
36. Zwicky, F., *Helv. Phys. Acta* **3**, 269, 466 (1930); *Proc. Nat. Acad. Sci.* **15**, 253, 816 (1929).
37. Miller, R. F., and Milligan, W. E., *Trans. A.I.M.E.* **124**, 229 (1937).

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The Mechanism of the Wetting of Textiles*

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Abstract

Consideration is given to the implications of the data on the wetting of textiles that are obtained by the use of a hydrometer method. This method permits a much more detailed study of the wetting process than is possible by the more usual methods. Some effects of rate of immersion of skeins of gray cotton yarn, skein density, solution temperature, and mechanical action are described.

This work suggests a resolution of the wetting of textiles into two independent processes. One of these, the escape of occluded gas, is essentially mechanical. The other, the rate of advance of the liquid phase into the mass to be wet, is a physicochemical problem.

Some studies of the time-dependence of the surface tension of solutions of surface-active agents are also described and discussed. It appears that the rates of surface-tension lowering correlate quite well with wetting-agent performance.

BECAUSE of the complex nature of the wetting process, as applied to textiles, it has been difficult to establish any close correlation between the physicochemical properties of wetting agents and their performance in wetting tests [6]. A possible way out of this difficulty has been suggested by some recent studies.

This recent work indicates that the wetting process can be resolved into two independent elements which are often competitive with one another. One of these, the escape of occluded gases, is essentially mechanical and therefore is primarily the concern of equipment and process engineers. The other, the rate of advance of the liquid phase into the mass to be wet, is the part of the problem which should be dealt with by physical chemical methods.

In support of this idea, two groups of experiments are here described. One involves the use of a previously reported hydrometer method [4] for studying the wetting of textiles. The other is an

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application of a film-balance technique [5] to the study of the time-dependence of the surface tension of wetting-agent solutions.

Bartholome and Schafer [1] have independently arrived at a similar conclusion. The experiments and discussion here are different, however, and their work and the present are somewhat complementary.

Escape of Occluded Gas

By attaching a sample of yarn or fabric to an appropriately designed hydrometer (Figure 1), it is possible to make rather detailed observations on the progress of the wetting process. Some of these observations, which have been described elsewhere [4], showed that when high concentrations of wetting agent are used, rapid but incomplete wetting is obtained. Representative data on the wetting of 5-g. skeins of gray cotton yarn are shown in Figure 2. The horizontal broken lines *A*, *B*, and *C* on this and subsequent figures represent, respectively, the buoyancy corresponding to the end-point of the Draves test [2] when a 3-g. weight is used; zero buoyancy, corresponding to the sinking of an unloaded sample; and the calculated buoyancy of a completely wet skein. The crossings of the time-buoyancy curves are due to the occlusion of larger quantities of air when the wetting of the outside yarns takes place rapidly.

Somewhat similar observations, obtained without the hydrometer, had been published in connection with the wetting of wood [9]. In that case, however, the less complete wetting by wetting-agent solutions as compared with pure water was attributed, possibly incorrectly, to the lower capillary rise of the low surface-tension solutions.

In the present work, some rather obvious elaborations of the earlier hydrometer experiments are described. Effects of the rate of skein immersion, skein density, temperature, and mechanical action were studied.

Rate of Immersion

The earlier experiments using the hydrometer method involved dropping the skeins into the wetting solution in a manner similar to that used in the Draves test [2]. The rapid immersion was conducive to the occlusion of air. The first group of new experiments therefore consisted in systematically varying the rate of skein immersion. The operator carefully lowered the hydrometer and skein into the wetting solution at a uniform rate so that the elapsed time from the beginning of the wetting to complete skein immersion had a preselected value.

The dramatic effect on the wetting which is produced by the variation of the rate of immersion is

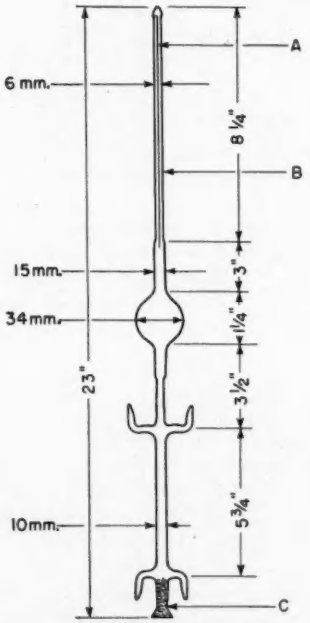

FIG. 1. *Hydrometer.*

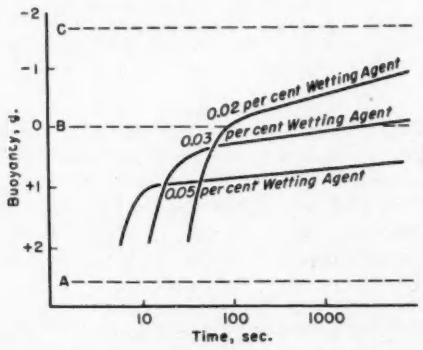

FIG. 2. *Time-buoyancy curves; 5-g. skeins of gray cotton yarn.*

shown in Figure 3. Notice that distinctly higher degrees of wetness are attained when the skein is immersed slowly. Presumably, this result is produced by the less effective occlusion of air in the slowly immersed skeins. Figure 4 shows that essentially the same result is obtained when higher concentrations of wetting agent are used. At lower wetting-agent concentrations (Figure 5), smaller volumes of air are occluded so that the effect of slow immersion is masked to some extent.

Skein Density

Since many practical applications of wetting-agent solutions involve more tightly packed yarns than those in the Draves skein, the second group of experiments were designed to permit observation of the effect of skein density. Three different degrees of packing were compared. These were achieved by braiding the Draves skeins with varying tightness. The relative densities of the braided and unbraided skeins are indicated in Figure 6, where the buoyancies of the skeins in pure water are shown.

Figure 7 shows that the effect of skein density is qualitatively similar in solutions of relatively high wetting-agent concentration and in pure water.

Figure 8 shows the intricate crossings of the time-buoyancy curves for the various skein densities when immersed in dilute wetting-agent solutions, which lead to the apparent similarity of the effects observed under the extreme conditions.

Quantitative interpretation of the skein-density experiments is complicated by the profound changes in skein geometry which are produced by braiding. It was most convenient, however, to hold the weights of the skein constant in these exploratory experiments. The work of Shapiro [8] on woven tapes, in which a balance was used in place of the hydrometer, does not appear to be detailed enough to be helpful in this connection.

Higher Temperatures

The use of wet processing solutions for textiles at higher temperatures is quite common. Hydrometer experiments conducted in hot solutions (75°C) again show the effect of occluded air. Notice in Figure 9 that the relative buoyancies at first reproduce the low-temperature observations. Later, however, the buoyancies of the immersed skeins increase with time. The increase is due to the increased gas volume which accompanies the rising temperature and

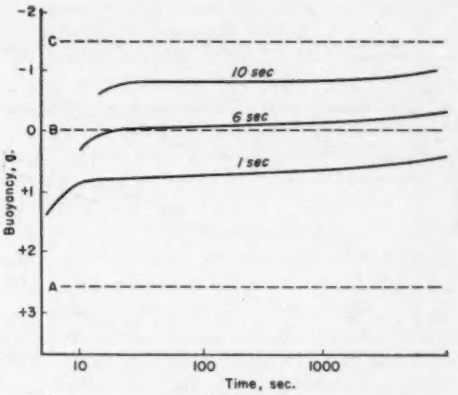

FIG. 3. *Rate of immersion study; 0.2% wetting agent.*

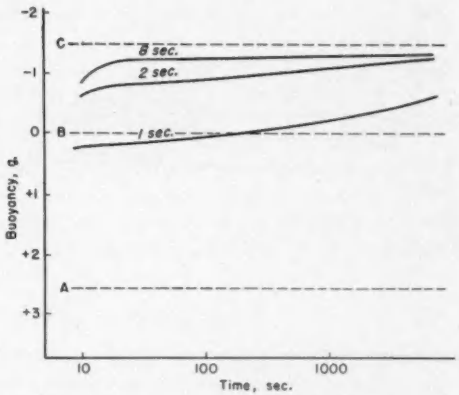

FIG. 4. *Rate of immersion study; 2.0% wetting agent.*

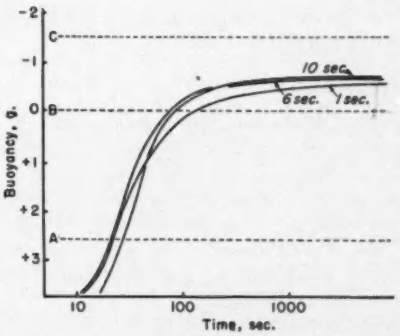

FIG. 5. *Rate of immersion study; 0.05% wetting agent.*

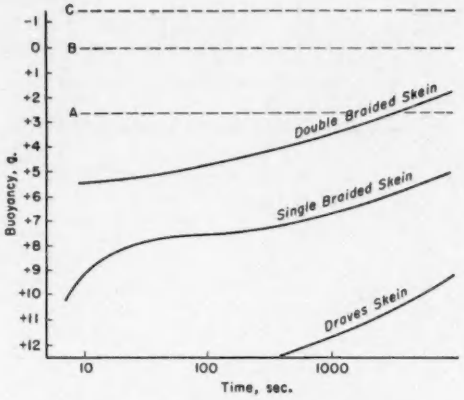

FIG. 6. *Skein density study; distilled water.*

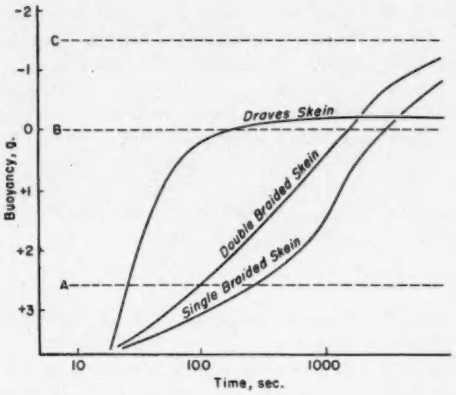

FIG. 8. *Skein density study; 0.02% wetting agent.*

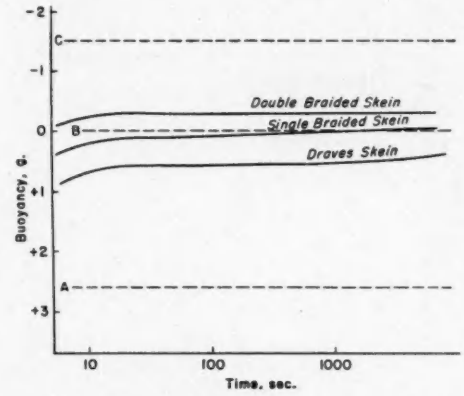

FIG. 7. *Skein density study; 0.4% wetting agent.*

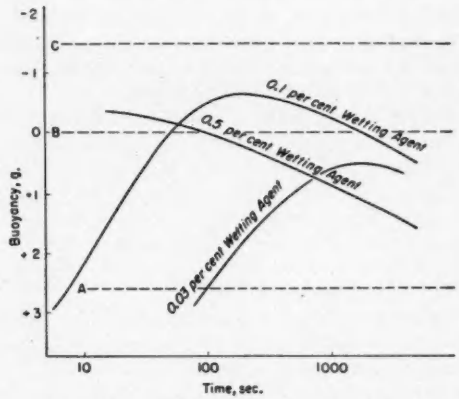

FIG. 9. *Elevated-temperature experiment.*

which arises from both gas expansion and the higher water-vapor pressure of the hot solution.

Mechanical Action

Agitation of the liquid in a wet processing bath for textiles and mechanical working of the mass to be wet are certainly favorable to the escape of occluded gas, and therefore also favorable to more complete wetting. In the present work, these factors were not studied directly, but some experiments were done which indicate that the occluded gas is quite difficult to dislodge.

A hydrometer jar was set up in such a way that the space above the liquid could be evacuated. The evacuated space was large enough so that the skein and hydrometer could be suspended in it. Provision was made for dropping the hydrometer and skein from the evacuated space into the liquid without breaking the vacuum. After the skein was immersed, the vacuum (25 in. of mercury) was repeatedly broken and reestablished. This caused a substantial flexing of the skein, as is shown by the buoyancy data in Figure 10 (the pressure and volume changes are approximately sixfold).

Two details of this figure are noteworthy. First, in spite of the rather severe flexing of the skein, which contains considerable occluded air, only a very small amount of the gas escapes as a result of the

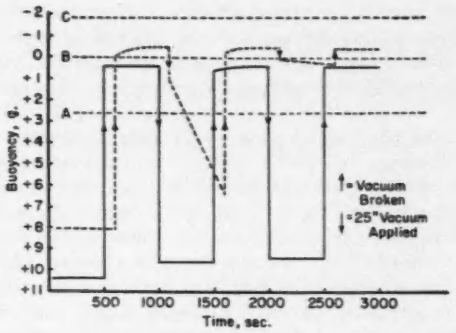

FIG. 10. *Mechanical action study; 0.1% wetting agent.*

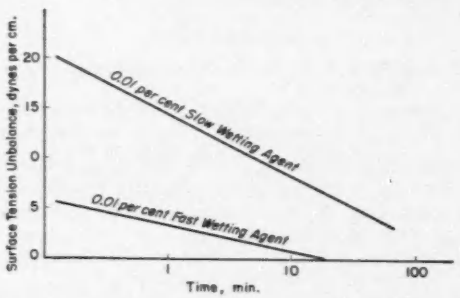

FIG. 11. *Time-dependence of surface tension.*

vacuum-pressure cycling. The other feature, shown by the dashed curve, is that the wet skein may have considerable rigidity and does not always permit the occluded gas to expand immediately in response to the application of the vacuum. Of course, the expansion does take place if sufficient time is allowed.

The experiments were too limited to provide a basis for discussing the unusually high buoyancies of the skeins immersed in wetting-agent solution using the evacuated system. The effect, however, appears to be reproducible.

Discussion of Hydrometer Experiments

The details of the wetting process which have so far been revealed by the use of the hydrometer method show clearly that the escape of occluded air can be a decisive factor in the effective wetting of skeins. The marked effect of rate of immersion suggests that technologically important results might be achieved by such simple devices as allowing a fabric to enter a wet processing bath obliquely, rather than normally, to the liquid surface.

Mechanical working of the immersed material as a device for facilitating the escape of air has yet to be reported in much detail. It is possible that experiments in which the escape of gas is observed directly with some sort of eudiometer arrangement would produce further interesting results in this connection.

The fact that less thorough wetting is achieved with higher concentrations of wetting agents highlights the competition between the escape of gas and the advance of the liquid. In other words, once the exterior of a mass of fibers is well impregnated with liquid, it becomes quite impermeable to gas. The experiments conducted at high temperature show that the occluded gas can expand the skein and possibly even force liquid, which has already penetrated, out of the fiber mass.

Advance of Liquid

From the equilibrium point of view, the conditions for the spreading of any of the common soap or wetting-agent solutions on textiles are quite favorable. The enormous difference between the performance of the stearic acid soaps and some of the new synthetic wetting agents in wet processing of textiles therefore suggests strongly that the dynamics of the process are important.

Film-Balance Experiments

When a mass of gray cotton fibers is immersed in a solution of a surface-active material, a large amount of new liquid surface is produced. This new surface initially has the composition of the bulk of the solution rather than the equilibrium surface composition, and its properties can be very different from those observed at equilibrium. The properties of newly formed surface of such solutions, as compared with equilibrium surfaces, are shown in Figure 11. The data were obtained using the film-balance method [5].

Figure 11 shows clearly the difference in surface dynamics observed when a relatively poor wetting-agent solution is compared with a relatively good wetting-agent solution. The experiment involved equilibrating the solution of the surface-active agent in a conventional film balance for several hours, and then sweeping the solution on one side of the pressure-sensitive barrier so as to produce a new surface.

The surface tension of the new surface at any time is equal to the equilibrium surface tension plus the observed tension unbalance. Similar experiments have also been reported recently by Bartholome and Schafer [1]. Other citations are also available [7].

While these rates of surface equilibration appear to be extremely important in wetting, the quantitative aspects of the problem are much more complicated because during wetting new surface is constantly being formed as the solution advances. Bulk diffusion in narrow capillaries and the depletion of small isolated volumes of solution with respect to the surface-active agent must also be taken into consideration. The good correlation between the performance of a wetting-agent solution and the time-dependence of its surface tension suggests, however, that the observed rates may be decisive. Further rate studies can be expected to be useful.

Discussion of Film-Balance Experiments

The factors which determine the rate of surface-tension lowering are quite complicated. However, one rather obvious consideration is the nature of the association of the molecules of the surface-active agent. In general, such molecules in aqueous solutions can go into the surface phase or, when all the surface sites are occupied, may associate to form micelles (see [6], p. 313). When new surface is formed, the free molecules in the solution are available to occupy the new sites, but these may have to be replenished by micelle decomposition.

The rate at which new surface sites are filled will then depend upon the number of free molecules in the solution, the rate of diffusion of these free molecules into the surface, and also the rate of micelle decomposition. On the basis of available data on surface-active compounds, the observed differences in rate of surface-tension lowering among the different preparations appear most likely to be due to differences in micelle stability and decomposition rates. Of particular interest in this connection is the work of Dreger, Keim, Miles, Shedlovsky, and Ross [3], who showed that branched-chain sulfates are more effective wetting agents than the straight-chain compounds. It is to be expected that the packing considerations which determine micelle stability become less favorable as the branching increases. Other information which conforms with this point of view is also available [6].

Literature Cited

1. Bartholome, V. E., and Schafer, K., *Melliand Textilber.* **31**, 487 (1950).
2. Draves, C. Z., *Am. Dyestuff Reptr.* **28**, 425 (1939).
3. Dreger, E. E., Keim, G. I., Miles, G. D., Shedlovsky, L., and Ross, J., *Ind. Eng. Chem.* **36**, 610 (1944).
4. Gruntfest, I. J., Hager, O. B., and Walker, H. B., *Am. Dyestuff Reptr.* **36**, 225 (May 5, 1947).
5. McBain, J. W., and Wilson, D. A., *J. Am. Chem. Soc.* **58**, 379 (1936).
6. Schwartz, A. M., and Perry, J. W., "Surface Active Agents," New York, Interscience, 1949.
7. Schwartz, A. M., and Perry, J. W., "Surface Active Agents," New York, Interscience, 1949, p. 286.
8. Shapiro, L., *Am. Dyestuff Reptr.* **39**, 38 (Jan. 23, 1950).
9. Stamm, A. J., and Petering, W. H., *Ind. Eng. Chem.* **32**, 809 (1940).

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Effect of a Dynamic Fatigue Test on the Mechanical Properties of Tire Cords

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Abstract

Changes in the mechanical properties of cords subjected to dynamic fatigue were measured for cotton, mercerized cotton, and rayon tire cords. These data were obtained by the use of an instrument which subjected the cords under tension to localized dynamic forces under controlled atmospheric conditions. The forces, when observed on an oscilloscope screen, were found to vary during the flex cycle. Flex life and ultimate elongation were found to be cumulative, regardless of whether the cords were fatigued continuously or were allowed to relax with or without static tension between periods of flexing. Calculated activation energies for fatigue failure were less than those for heat degradation. From the differences in properties a qualitative evaluation of tire cord behavior could be made.

THE FATIGUE-RESISTANCE of an automobile tire cord plays an important part in the performance of the tire. A tire in service must endure periodic and unequal stresses, relaxations, and compressions under varying conditions of moisture and temperature. The ability of the cord, the unit supporting structure of the tire wall, to withstand these varying forces depends upon its physical properties —its strength, elongation, and elastic behavior. While much has been reported in the literature about the effects of the forces on these properties, the interpretation of this type of information in terms of tire performance is still in the experimental stage.

The previous interpretations have been made on the basis of data on the dynamic fatigue obtained on testing machines of radically different designs [1, 2, 7, 12, 14, 19, 20, 25, 27]. But since none of the available machines was considered sufficiently reliable to be accepted as the standard by the American Society for Testing Materials, a special instrument was constructed for the present work which bends cords while subjecting them to localized dynamic-fatigue factors. This machine provided a means of comparing the changes undergone in strength, elongation, and energy characteristics by cotton, mercerized cotton, and rayon tire cords after fatiguing under different conditions. The results, after the necessary limitations of the test are taken into account, indicate a characteristic pattern of performance for each of the materials examined.

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The Instrument

Description

The multistand flexing instrument, which permits simultaneous testing of as many as 8 specimens, is illustrated in Figure 1. Each of 4 testing units consists of the following: the support and flexing unit, *A*, with frame, self-locking cord clamps, tensioning springs, and paired plastic pulleys; the oven, *B*, for maintaining a constant atmospheric condition; and the drive mechanism, *C*, of motor and eccentrics. A humidification tank, *D*, controls the moisture conditions in the 4 ovens.

The essential parts of the flexing unit and an enlargement of the self-locking clamps with a cord in place are shown in Figure 2. The cord, *h*, held by the upper clamp, *a*, is passed between 3 pairs of heat-resistant, smooth-surfaced plastic pulleys, *b*, *c*, and *d*, and is held at its lower end by clamp *e*. Pairs *b* and *d* are rigidly attached to the supporting frame (Figure 1), while pair *c* is attached to the end of the lever, *l*. The lower clamp is guided by the shaft, *f*, to transmit tension applied to the cord by a torsional spring, *s*. The lever, *l*, with pivot at *p*, is driven with reciprocating motion by an eccentric, *g*, connected through reducing sheaves to a constant-speed motor. Lever strokes are registered on the

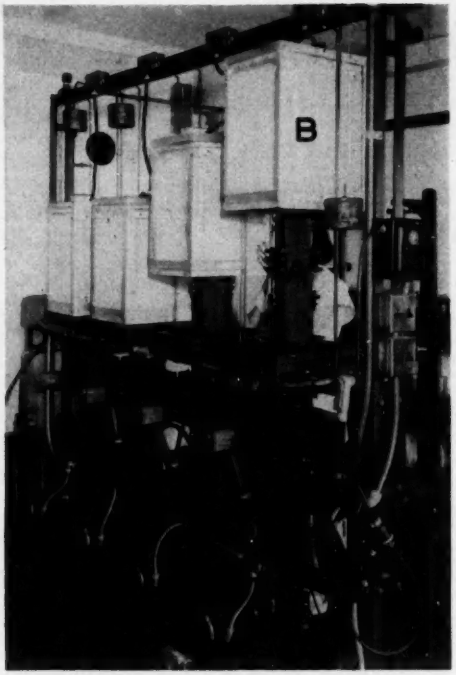

FIG. 1. *Photograph of multistand flexing instrument.*

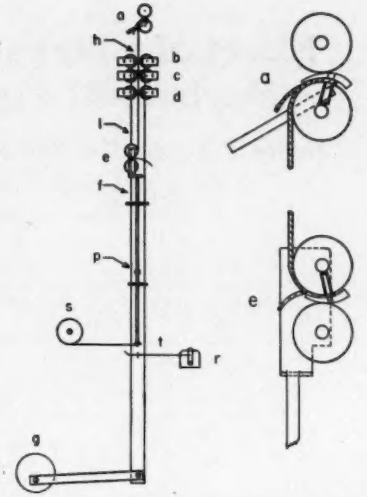

FIG. 2. *Schematic diagram of flexing unit. The cord,* h, *is held by clamps,* a *and* e, *with tension applied through guide shaft,* f, *by springs,* s. *Pulleys* b *and* d *are fixed. Pulleys* c *move with lever,* l, *pivoted at* p *and driven by eccentric,* g. *The counter,* r, *connects to the lever through arm* t.

counter, *r*, until cord failure permits the spring arm to disengage the counter connection, *t*. Load is applied by a 10-in. arm projecting at right angles from one end of a cylindrical spring in torsion; the opposite end of the spring is equipped with a dial and ratchet to adjust tension.

The oven of each unit (see Figure 1, *B*), which is similar to an oven described in an earlier publication [10], encloses the flexing mechanism and is counterbalanced to permit raising and lowering. Each oven is constructed from impervious 2-in. insulation blocks sealed together with waterproof cement and is protected by a coating of aluminum paint and by a welded frame of $\frac{3}{4}$-in. angle iron on the edges. The inside dimensions of the oven are 8 in. × 12 in. × 18 in. The base of the oven is rigidly attached to the supports. Different-sized openings are provided through which the moving parts enter the oven. The oven is heated by two 110-volt heating elements constructed from 18 ft. of 4 ohm/ft. resistance wire attached to the 12 in. × 18 in. inside wall. A mercury thermoregulator inserted through the top controls the temperature within ± 1°C over the range between 25° and 160°C.

The humidification tank (Figure 1, *D*), used to control the moisture conditions in the 4 ovens, is constructed from $\frac{1}{4}$-in. iron, is 12 in. in diameter, 24 in. in height, and is insulated with a 2-in. thickness of hot-pipe asbestos. Two 500-watt heaters, inserted opposite each other about 2 in. above the bottom, heat water in the tank. A thermoregulator inserted in a well through the side actuates the heating circuit to control the temperature of the water within ± $\frac{1}{2}$°C. Compressed air at 4 lbs. pressure enters the tank from either side directly below the heaters and bubbles from perforated pipes through 14 in. of water, striking baffles in its path through the water and space above. A heated pipe inserted in the top of the tank carries the humid air through two orifices extending from the base of each oven. This air stream, in addition to determining the dew point, prevents temperature stratification in the oven. Water temperature below room conditions is obtained by pumping iced water through copper coils between the water surface and the heating elements. By

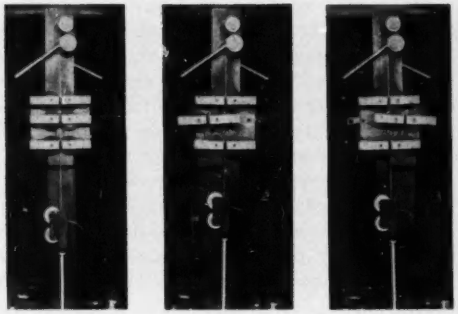

FIG. 3. *Position of pulleys: 1—loading position; 2 and 3—extreme positions.*

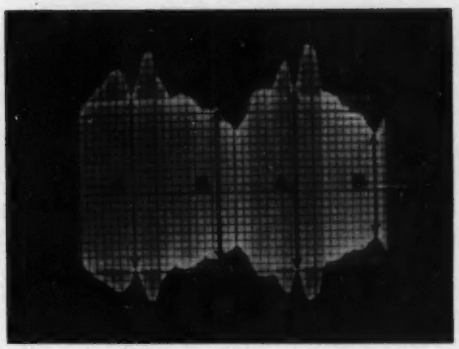

FIG. 4. *Oscilloscope pattern of force differences during flexing.*

changing the temperature of the water, a wide range of moisture conditions may be obtained. Even lower temperature or moisture conditions may be obtained by passing the air through coils immersed in low-temperature mixtures such as dry ice and acetone.

Principles of Operation

While the pulleys are in the loading position (Figure 3, *1*) cords are inserted in the clamps of the machine. Then the ovens are lowered, and the mounted cords are allowed to condition in the testing atmosphere for 10 min. During this conditioning period, the cord supports only the weight of the lower clamp, 2.2 oz. The testing load is then applied, instantaneous elongation occurs, and the cords are permitted to creep for 5 min. before flexing. The cords are flexed into arcs around pulleys which rotate with the cord to reduce abrasion. When pulleys are in the extreme positions, as indicated on stands *2* and *3* in Figure 3, the lower clamps have been pulled upward by the tortuous path of the cord. An approximately constant tension is maintained by the spring arm following the motion of the lower clamp. In order for failure to be a measure of flexure endurance, it had to occur on that section of the cord which contacted the periphery of the pulleys. Failure on any other section was excluded in the consideration of results.

Test Conditions

As required in the routine testing of materials, the effect of variables in use of this testing instrument was minimized by the adoption of certain operating standards which reasonably simulated service conditions and yet were practical for laboratory operation in regard to length of time for a test. After a certain amount of preliminary investigation, a 10-in. specimen length, pulleys 1 in. in diameter, and a flexing amplitude of 1 in. at the rate of 250 cycles per minute were selected. These constants prevailed in the present work unless specifically stated otherwise.

Many reports are given in the literature on the influence of changes in test conditions on the properties of cords [3, 4, 6, 8, 13, 16, 22, 23, 24, 26]. Hence, the multistand instrument was constructed to permit tests over a range of loads and atmospheric conditions. The applied load ranged from 2.5 to 10 lbs., the lower load limited by the inertia in the system and the higher by the capacity of the spring. Comparisons of the flexure endurance properties of different cords were made under loads of equal percentages of their individual conditioned strength. The temperature limits of this instrument were from below 0° to 160°C, with dew points from − 60° to approximately 100°C. In routine determinations for oven temperatures of 27°C and above, dew points were maintained at 23°C. At an oven temperature of 27°C the moisture content of the cord approximated that at standard conditions (70°F, 65% R.H.).

When the dynamic forces applied to the cord were studied in another investigation,* variations were found which were dependent upon the position of the pulleys during the flex cycle. Figure 4 is a photo-

* Manuscript in preparation.

TABLE I. PHYSICAL CHARACTERISTICS OF TIRE CORD SAMPLES

Characteristics	Cotton	Mercerized cotton	Rayon
Construction	17.5/4/3	17.5/4/3	1100/2
Twist per inch			
Singles	9.90Z	10.66Z	—
Ply	20.30Z	18.07S	14.20Z
Cord	9.90S	9.66Z	10.51S
Thickness (in.)	0.0304	0.0296	0.0228
Cord number (cotton system)	1.19	1.22	2.09
Breaking load (lbs.)			
70° F, 65% R.H.	25.5	22.6	13.4
224° F	24.4	23.4	17.2
Elongation at break (%)			
70° F, 65% R.H.	9.7	9.5	14.2
224° F	7.8	8.9	10.6
Tenacity (g./grex)	2.33	2.12	2.15

graph showing the magnitude of the forces transferred to the oscilloscope screen from an energized differential linear transformer and proving ring [21]. As the pulleys crossed position *1* (Figure 3), the amplitude of the background and pattern at *A* represent the load on the cord when under static tension. The stresses at the ends of the flexing arcs are indicated by *B*. The maximum forces occurred immediately after *A*, and the minimum after *B*. Since the duration of a complete cycle was approximately $\frac{1}{4}$ sec., forces and partial relaxations were completed in short intervals, the time element of which is comparable for variations in forces in a tire while operating at normal rates of speed [18].

While a tire may be subjected to intermittent dynamic forces during road use and continuous static forces when stationary, routine tests have been made only for dynamic fatiguing without interruption. A preliminary comparison of results from continuous flexing and intermittent flexing, both with and without static loads during the relaxation-from-flexing periods, has shown no significant difference in results for flex life and for ultimate elongation. The continuously fatiguing treatment was therefore selected as being more practical for the laboratory tests because of the time element.

Statistical Reliability

The type of distribution of number of flexures endured and the number of observations for a test are important in the determination of the significance of results. In a preliminary investigation into the variations and reliability of results obtained from this instrument, 225 observations were made at 120°C on a cotton cord; the coefficient of variation was found to be 25%. While the number of flexures endured was skewed toward the higher values, the *chi*-square test did not exclude the data from consideration as a normal distribution.

The data presented herein were obtained from a test of 15 individual specimens. For this number of observations, if the coefficient of variation were 25%, the uncertainty would be 12% at the 90% level. However, the amount of spread in individual observations was dependent upon factors in the test such as load and temperature as well as uniformity of material. The range for coefficients of variation in normal testing was between 20% and 30%, with higher coefficients found when the period of endurance was very short.

Samples

Cotton, mercerized cotton, and rayon tire cords were the materials examined. The characteristics and physical properties of the cords are given in Table I. The cotton and the mercerized cotton cords were processed experimentally from Wilds 13 cotton of $1\frac{3}{8}$-in. staple length on regular commercial equipment. The stretching procedure was the same for both of these cords; however, the direction of twists differed. The mercerization was done at the yarn stage, with shrinkage controlled at 8%. The rayon cord was made from high-tenacity viscose filaments, and was obtained from regular production.

Flex Life

Relation to Load

The flexure endurance-load relationship was investigated over the range of the instrument. The curves (Figure 5) indicate that, generally, at a constant temperature the relationship between tension and logarithm of mean number of flexures is inversely linear. Because of this relationship, the endurance for a desired load may be obtained by a test at the particular load or, more often, by interpolation between results obtained from two adjacent loads. However, deviations from this general relation will be noted for certain materials at particular test conditions. For the mercerized cotton cords at the lower loads, the relationship was linear, but became slightly curvilinear in the region of the higher loads. This departure from linearity was probably

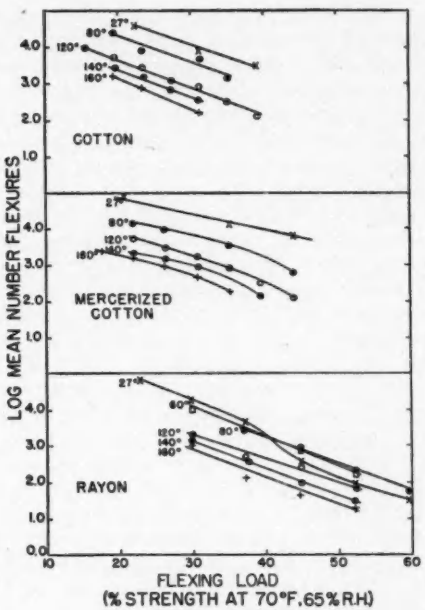

FIG. 5. *The effect of load and temperature (°C) on flexure endurance.*

due to the moisture-strength-time relationship peculiar to a cord of this type of material. For the rayon cord tested at room conditions, the critical change in the region of about 40% load was comparable to the point of inflection which occurs on the load-elongation curve for rayon cords.

Relation to Temperature

When the effect of temperature on flex life was investigated over a large range of loads (Figure 5) it was noted that, in general, an increase in temperature definitely decreased flex life. However, when the rayon cords were flexed at 27° and 60°C at loads above 35%, their flex life was less than the flex life for 80°C. This departure at the lower temperatures from the general relationship was probably due to the changes in physical properties of rayon tire cords with moisture. In Figure 6 are given the flexure endurances of the samples as a function of the reciprocal of absolute temperature between 160° and 27°C for an interpolated load of 31%. It may be seen that the logarithm of the mean number of flexures was linear with the reciprocal of

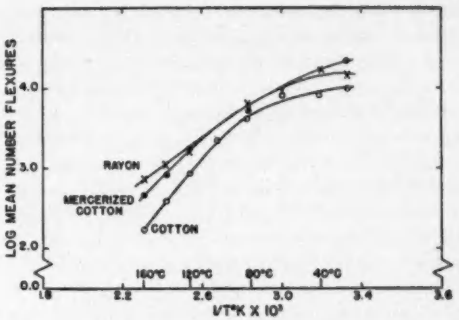

FIG. 6. *Flexure endurance under comparable load as related to temperature (1/°K).*

absolute temperature from 160° to about 100°C. As temperature decreased to 27°C, flexure endurance increased, but at a slower rate than at the higher temperatures.

In studying the decrease in fatigue endurance with increase in temperature, others [3, 27] used the Arrhenius equation [9] in the interpretation of their results, and found that the calculated activation energy varied with the parameters of their test. In basic tests on rayon, they obtained values approximating the value for the heat degradation of cellulose. In a special test with altered parameters (condition B), Waller and Roseveare obtained activation energy which was significantly smaller than the values for the basic tests. Hence, they concluded that, for dynamic fatigue, the parameters of the test alter the relative importance of factors of degradation.

The Arrhenius equation [9], $\ln L = E/RT + C$, was also applied to the data obtained from the present instrument for temperatures above 100°C. In the equation, L represents the number of flexures; E, the energy of activation; T, the absolute temperature; R, the gas constant; and C, a constant. The values obtained for energy of activation are given in Table II. It will be noted that they are significantly

TABLE II. ACTIVATION ENERGIES OF CORDS

Cord	Activation energy (cal./kinetic unit)
Cotton	13,600
Mercerized cotton	11,000
Rayon	7,700

smaller than the established value for the heat degradation of cellulose—*i.e.*, 25,000 cal./kinetic unit [5, 27]. The energy of activation for the rayon cord in the present work was of the same magnitude as the value obtained by Waller and Roseveare in their special test (condition B) [27]. In a supplementary temperature study, 3 cotton cords of a 22.70/4/3 construction were fatigued, and calculated energies of activation were found to be 15,800, 15,400, and 14,500 cal./kinetic unit. These values are also smaller than the value generally accepted for the heat degradation of cellulose. From these consistently small values for activation energy, it has been concluded that factors in addition to heat are responsible for the failure of cords.

Below 100°C, moisture content and the chemical composition of the cord became more important factors in flexure endurance. As temperature approached normal room conditions, there was an overall increase in flexure endurance. Since there was an increase in the moisture content of the cord with the decrease in temperature, there was evidence of increased flexure endurance for cotton at temperatures below room conditions. However, in rayon cords, flexure endurance approximated a maximum at temperatures slightly above room conditions.

Cord Properties after Flexing

After subjection of these cords to dynamic forces, an investigation was made into the changes in their mechanical properties. Cords were flexed at 27°C for various percentages of their average flex life; they were dismounted after flexing and allowed to relax under standard atmospheric conditions. After relaxing for at least 20 hrs., tensile tests were made on a pendulum-type tester on only 8 in. of the original specimen so as to exclude that part which had been held by the clamps during flexing. The retained strengths and elongations were read from the load-elongation curves, and the remaining energies were recorded as the areas under the curve [11]. In Table III are given the data on three properties of the cords, expressed as percentages of the corresponding value for the unflexed cord. In general, the coefficients of variation obtained from flexed cords were larger than those from the unflexed cords.

Even though some of the cords had begun to fail during the longer flexing periods, the selected specimen number, 15, was retained by flexing additional cords. During the longest flexing period, 24% of the cotton and 12% of the mercerized cotton cords failed. However, 20% of the rayon cords failed in the next to the longest period, but none failed in the longest. Due to the fact that it was impossible to determine changes in the properties for the failed cords and that it was necessary to flex additional cords in order to fulfill the requirements for the test, a bias was introduced which favored the surviving cords. This is probably reflected in results for the cotton cord flexed for the longest period.

Small gains in breaking load due to the initial flexing period were found for mercerized cotton and rayon cords; the cotton cord reached a maximum, but from a shorter period of flexing. Similar increases were found when cords were subjected to static load. After comparable periods of flexing, the loss of strength by the cotton and the significantly smaller loss by rayon cords would indicate that retained strength alone is a questionable basis for comparing cords of different materials unless the differ-

TABLE III. PHYSICAL PROPERTIES OF FATIGUED CORDS

Identification	Before fatigue	Remaining flex life 100%	90.6%	81.1%	71.7%	62.3%	52.8%	43.4%
Cotton								
Breaking load	26.3 lbs.	100	100.0	98.1	95.1	90.9	87.5	89.0
Elongation at break	10.5%	100	89.5	83.8	82.9	77.1	73.3	77.1
Energy		100	83.0	77.3	73.6	66.5	61.0	64.6
Cotton, mercerized								
Breaking load	24.3 lbs.	100	101.6	100.0	95.1	90.9	88.1	87.2
Elongation at break	11.3%	100	80.5	76.1	72.6	70.8	68.1	62.8
Energy		100	75.6	69.9	63.3	61.0	55.8	50.6
Rayon								
Breaking load	13.5 lbs.	100	103.7	104.0	103.0	100.0	99.3	97.8
Elongation at break	14.2%	100	80.3	78.9	75.5	73.9	73.2	71.1
Energy		100	77.4	75.0	72.6	67.4	67.0	63.6

ences in rates of decrease in strength with flexing for the materials are recognized.

From the data presented in Table III, it may be stated that there was a rapid change in elongation to break during the initial dynamic periods, followed by a gradual decrease in rate of change as the dynamic period was extended. When 43.4% of their average flex life remained, breaking elongations of the cotton and rayon cords were not significantly different; breaking elongation of mercerized cotton cords was significantly more than for either of the other cords. Part of the creep from flexing was not recoverable, and the longer the flexing period, the greater the irrecoverable elongation, with variations dependent upon the cord material.

Within the range tested, a linear relationship was obtained between percent retained energy and percent remaining flex life, the two cotton cords having the greater slopes. But the cords were in a relaxed state, and all of the values for energy would have been smaller had they been tested before relaxation.

Intermittent Fatiguing Effects

The results and relationship which have been presented so far were obtained from tests of cords which were flexed continuously. However, this is not typical fatigue wear for tire cords in actual service, where they are subjected intermittently to dynamic fatigue and relaxation. To justify the use of such data for evaluating tire-cord properties, and to follow elongation changes as tire cords fatigue, a study was made of flexure endurance and elongation when cords were flexed and relaxed alternately until failure occurred. In one set of observations, the static load was allowed to remain on the cord during the relaxation-from-flexing period; in another, the static load was completely removed, the cord being thus free of tension during the relaxation period. For the latter case, immediately before the beginning of each flexing period, the cord in loading position was subjected to the regular 5 min. of static load for mechanical conditioning of the cord. The periods of flexing were selected to be equivalent to 20% of the flex life of the particular type of cord, with intervening periods of relaxation, such that failure occurred in 3 days. These tests were made under a 23% load, with oven temperature at 27°C.

Comparisons were made between the results from the 2 types of intermittent flexing and those from the continuous flexing. No significant difference in total flexure endurance of the cords from the same material was found among the 3 conditions of fatiguing. This irreversibility of fatigue from flexing was in accord with the findings of Busse [3].

In Figure 7 the elongation of these cords is shown for the 3 conditions of fatiguing: curve *A* shows elongation when the cord was flexed continuously to failure; curve *B*, when the cord was flexed intermittently, with the load remaining during the relaxation period; curve *C*, when the cord was flexed intermittently, without load during the relaxation period. If the regular static period, as shown in Figure 6, had been allowed to continue, it would have followed the usual exponential relation [15, 17, 26]. The second period of elongation, which occurred during flexing, was linear with log flexures over the greater portion of the curve, but departed from this relationship as cord rupture became imminent. Regardless of whether the cord was flexed continuously or intermittently, the total elongation was essentially the same. However, from Figure 7 it is apparent that there was slightly greater elongation for *B*; this may be attributed to the primary creep within the cord when held under continuous load for the total period (3 days). During any flexing period, the amount of elongation for a particular type of cord is dependent upon the type of fatiguing treatment and upon the amount of flexing previously endured. For *B* and *C*, the total elongation during any particular flexing

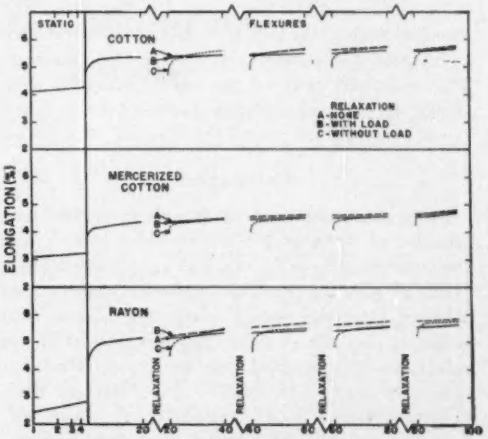

FIG. 7. *The elongation of cords as related to fatigue life.*

period was equal to the elongation recovered during the previous relaxation period plus the elongation characteristic of this particular stage in the flex life of the cord. As the percentage of flexures endured increased, the amount of recovered elongation during the relaxation period and the elongation from flexing decreased, with an accompanying increase in the rate of return to the amount of elongation at the end of the previous flexing period. However, in the final flexing period there was a decided increase in the slope of the elongation curve, which indicated an increase in the deterioration rate of the cord itself. It will be noted that the total elongation of these flexed cords was less than the elongation at break (Table I). This is easily understandable, because these cords were subjected to fatiguing treatments differing over sections of their length, and rupture occurred from weakness in the flexed section before an elongation comparable to that of a tensile test had been reached. While the rates of elongation differed among cords, their responses to the 3 conditions of flexing fatigue followed similar patterns.

Photomicrographs of Ruptured Fibers

When photomicrographs were made of fibers from the flexed section of a fatigued cord, two types of failure were found. The majority of the fibers exhibited breaks which resembled those typical for tensile tests. However, throughout the section were found breaks, as shown in Figure 8, which seemed to be characteristic of the material of the cord. The damaged ends of the cotton fibers showed a shredded appearance that is typical in damage from abrasion. The splintered ends of the rayon filaments were similar to photomicrographs published for fatigued rayon fibers [27].

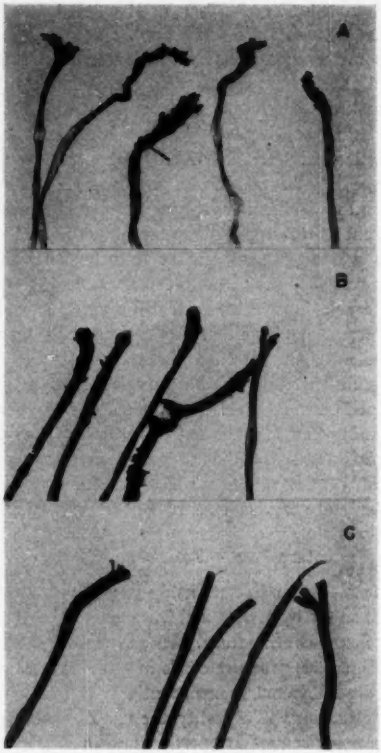

FIG. 8. *Photomicrographs of damaged fibers from ruptured section of fatigued cords. A—Cotton. B—Mercerized cotton. C—Rayon.*

Conclusions

From these investigations into the properties and behavior of cords from 3 different materials, a pattern characteristic of the material was obtained which primarily gave the trends and ranks of fatigue results obtained from the testing instrument. Since cord fatigue is only one of the contributing factors in tire failure, no attempt should be made to correlate flex results on cords with road or wheel tests on tires. Results obtained from fatiguing cords before vulcanization in a tire are at best only a partial approximation for predicting performance of the cord in the tire. The quantitative data obtained from testing tire cords on this instrument cannot be used as absolute, but they are usable for qualitative evaluations of cord properties. The instrument offers a rapid means for preliminary ranking of cords tested at conditions reasonably resembling those encountered by the tire cord in service.

Acknowledgment

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Literature Cited

1. Bradshaw, W. H., *ASTM Bull.* No. 136, 13–17 (1945).
2. Budd, C. B., and Larrick, L., *ASTM Bull.* No. 136, 19–25 (1945).
3. Busse, W. F., Lessig, E. T., Loughborough, D. L., and Larrick, L., *J. Applied Phys.* **13**, 715–24 (1942); correction, *ibid.*, **16**, 120 (1945).
4. Conrad, C. M., Lyons, W. J., and Tripp, V. W., TEXTILE RESEARCH JOURNAL **16**, 324–8 (1946).
5. Conrad, C. M., Tripp, V. W., and Mares, T., TEXTILE RESEARCH JOURNAL **21**, 726–39 (1951).
6. Dillon, J. H., and Prettyman, I. B., *J. Applied Phys.* **16**, 159–72 (1945).
7. Fromandi, G., Proc. 2nd Rubber Tech. Conf., Cambridge, England, W. Heffer & Sons Ltd., 1948, pp. 464–77.
8. Fuwa, T., *Textile World* **64**, 3577–81 (1923).
9. Glasstone, S., Laidler, K. J., and Eyring, H., "The Theory of Rate Processes," New York, McGraw-Hill, 1941.
10. Grant, J. N., *Rev. Sci. Instruments* **15**, 46 (1944).
11. Hamburger, W. J., TEXTILE RESEARCH JOURNAL **18**, 102–13 (1948).
12. Hershberger, A. (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,211,951 (Aug. 20, 1940).
13. Karrer, E., Grant, J. N., and Orr, R. S., TEXTILE RESEARCH JOURNAL **17**, 314–22 (1947).
14. Kenyon, J. N., U. S. Patent 2,328,908 (Sept. 7, 1943).
15. Leaderman, H., "Elastic and Creep Properties of Filamentous Materials and Other High Polymers," Washington, D. C., Textile Foundation, 1943.
16. Lewis, W. S., TEXTILE RESEARCH JOURNAL **17**, 431–7 (1947).
17. Lyons, W. J., *J. Applied Phys.* **17**, 472–82 (1946).
18. Lyons, W. J., and Prettyman, I. B., *J. Applied Phys.* **19**, 473–8 (1948).
19. Mallory, G. D. (to Wingfoot Corp.), U. S. Patent 2,412,542 (Dec. 10, 1946).
20. Roseveare, W. E., and Waller, R. C., TEXTILE RESEARCH JOURNAL **19**, 633–7 (1949).
21. Schaevitz, H., *Proc. Soc. Exptl. Stress Analysis* **4**, 79–88 (1947).
22. Scholes, A., *J. Textile Inst.* **35**, P99–113 (1944).
23. Stoll, L., *Gummi-Ztg.* **43**, 2218–21 (1929).
24. Truesdale, R. A., *Textile Recorder* **40**, 52–4 (1922).
25. Venable, C. S., *ASTM Bull.* No. 136, 17–19 (1945).
26. Wakeham, H., Honold, E., and Skau, E. L., *J. Applied Phys.* **16**, 388–401 (1945).
27. Waller, R. C., and Roseveare, W. E., *J. Applied Phys.* **17**, 482–91 (1946).

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Sorption of Acid Dyes by Nylon Under Nonequilibrium Conditions

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Abstract

Nylon filament yarn colored with acid dyes frequently shows unevenness in appearance. In some cases this unevenness can be traced to slight differences in orientation due to uneven drawing. In other cases small changes in the number of amine end-groups in the polymer cause this effect. It has been found that this unevenness can be minimized, and with some colors completely eliminated, by dyeing in a bath so dilute in dye as to be colorless to the eye.

IN the coloration of natural fibers, such as wool, by sorption of dyes, equilibrium between dye on the fiber and dye in the bath follows, in general, the isotherm equation of Langmuir [5], especially near the limits of saturation of fiber with dye. Adjustment of the equilibrium to favor level distribution of dye on the fiber is usually accomplished by gradual heating of the bath and, in some instances, by addition of salt to the dye bath. The establishment of favorable equilibrium is a factor of great importance in equaliz-

ing the depth of dyeing throughout the fiber mass. Hence, for the most satisfactory dyeing, dyes are chosen that readily come to equilibrium; these are said to "boil off and on."

The same principles are applicable to the dyeing of nylon. With this fiber, acid dyes are attached by the same mechanism as with wool—*i.e.*, by salt formation between the dye and the basic amino end-groups in the fiber. However, nylon fiber differs from wool in that it sorbs acid dyes to a lower saturation level [1, 3]. Consequently, slight variation in amine titer in the yarn can lead to pronounced differences in appearance along the yarn after dyeing. Such an effect can also be caused by slight differences in the orientation of the polymer chains resulting from variation in the amounts of drawing to which the yarn is subjected after spinning. Yarns exhibiting these differences are said to lack "equalization" (this term distinguishes from level dyeing, which refers to absence of spottiness). In addition, many acid dyes do not readily "boil off and on" nylon. These differences in behavior present limitations to the usefulness of the equilibrium procedure for application of acid dyes to nylon.

In the course of a study of the mechanism of nylon dyeing, it was discovered that equalized dyeings can be produced by a procedure that is diametrically opposite to that used for wool. This procedure involves conditions that are as unfavorable as possible to the attainment of equilibrium—specifically, supplying dye to the fiber at a rate lower than the fiber is capable of sorbing it.

Experimental

Materials

For the experiments involving dye transfer from wool, a good grade of wool tops was first dyed with acid colors by conventional procedures.

The nylon samples used were of two types. The first was used for studying the effects of orientation. In this case, two samples of polyhexamethyleneadipamide nylon yarn differing by 4% in draw ratio were knit together to provide a junction of the two yarns in the center of the test piece ("draw-ratio junctions"). The second type was prepared in the same manner using yarns of the same draw ratio but differing in the amount of amine end-groups (these are referred to as "package junctions").

The dyes employed were commercial samples. Slightly soluble dye salts were prepared by addition of a solution of a salt of the precipitating cation—*e.g.*, barium chloride, calcium chloride, or lead acetate—to a solution of the dye.

The control dyeings, used to compare equalization properties, were prepared in all cases by dyeing the nylon piece at 90°C for 1 hr. in a bath in which the liquor/nylon ratio was 50 and to which 0.1% of glacial acetic acid had been added.

Dyeing by Transfer from Wool

Dyed wool and a nylon draw-ratio junction were heated together in boiling water for periods of 1–12 hrs. During this time the color on the nylon slowly

TABLE I. NYLON JUNCTIONS COLORED BY TRANSFER OF DYE FROM WOOL

No.	Dye used on wool*	Time of heating wool and nylon together (hrs.)	Dye depth† on nylon (%)	Junction rating‡
1	5% Du Pont Milling Red SWB	12	1.5	0
	Control for No. 1**		1.5	3–4
2	10% Du Pont Milling Red SWB	1.5	0.2	0
	Control for No. 2		0.2	4
3	5% Du Pont Neutral Brown 2RS	12	1.5	1
	Control for No. 3		1.5	4
4	3% Du Pont Anthraquinone Green G	1	0.5	0
	Control for No. 4		0.5	2–3
5	3% Du Pont Anthraquinone Violet R	3	0.1	1
	Control for No. 5		0.1	2–3

* Five grams of wool tops dyed in a 200-cc. bath containing 0.25 g. of glacial acetic acid. Two grams of the dyed wool were placed in a 300-cc. bath with a 2-g. knit nylon junction. Dyeing of the nylon was brought about by boiling this bath for the periods specified.

† Depth of color was determined by comparison with a conventionally dyed nylon piece colored from baths containing the dye percentages given. All percentages were based on the weight of the material to be dyed.

‡ Junction ratings were determined as follows: 0 = a junction in which a trained observer could not discern a shade-depth change; 1 = a junction in which the shade-depth change was so slight as to be the limiting case detectable by a trained observer; 2 = a junction in which the shade-depth change was twice as severe as a No. 1 junction; 3 = a junction in which the shade-depth change was three times as severe as a No. 1 junction; 4 = a junction in which the shade-depth change was four times as severe as a No. 1 junction.

** Control dyeings were made using conventional techniques.

increased, even though no color was visible in the bath. As is shown in Table I, complete equalization of draw-ratio junctions was obtained by this procedure with three out of five dyes tested. Further, improvement in equalization of the other two members of the series was outstanding since color-depth differences at the junction were just detectable visually as compared to severe differences in the control dyeings.

Dyeing by Controlled Addition of Dye [4]

An equally effective procedure for giving equalized dyeings involves the continuous addition of a solution of dye to a circulating colorless dye bath. For this purpose, a dyeing chamber was connected by means of a short tube to a pump whose outlet led to a 25-ml. chamber for mixing the dye bath with fresh dye solution. The outlet of this chamber was provided with a tube for continuously re-adding the dilute dye solution to the dyeing chamber. The total volume was about 150 ml.

In a typical dyeing, 0.1 g. of glacial acetic acid and 100 ml. of water were added to the dyeing chamber, followed by the addition of a 2-g. nylon section. The bath was then heated to 90°C and circulated by the pump at a rate sufficient to completely change the bath 6.5 times per minute. The dye to be used (see Table II), dissolved in 50 ml. of water, was added to the mixing chamber at a rate such that its presence was not detectable visually in the dye bath. The total time required for addition of dye was about 1 hr.

The results are shown in Table II, which illustrate the great improvements in equalization obtained by using several dye mixtures on either the draw-ratio or the package type of junctions. With one dye mixture the changes in color depth at the junction, shown by comparison with the control dyeings, were completely eliminated, and with the others the junction differences were so slight as to be almost nonexistent.

Dyeing with Sparingly Soluble Salts [2]

In a third method of obtaining equalized dyeings on nylon, sparingly soluble salts of acid dyes are employed. In this instance, the amount of color present in solution in the dye bath is restricted by the low degree of dissociation of the dye salt. For this purpose, barium, calcium, and lead salts of acid dyes were used.

Dyeings were conducted by dissolving the dye (see Table III) in 100 ml. of water, followed by addition of 0.1 g. of glacial acetic acid. To this solution was added, with stirring, 0.2 to 20 g. of either barium chloride, calcium chloride, or lead acetate. A dye-salt dispersion formed immediately. A 2-g. nylon

TABLE II. NYLON JUNCTIONS COLORED BY CONTROLLED ADDITION OF DYE

No.	Dye combination	Amount of dye used (%, based on nylon wt.)	Junction type	Time of dyeing (min.)	Junction rating*
1	Du Pont Neutral Yellow GS	0.12			
	Du Pont Neutral Brown 2RS	0.22	Draw ratio	65	0
	Pontacyl Fast Black N2B, Conc. 200%	0.035			
	Control dyeing for No. 1		Draw ratio	60	3–4
2	Same as No. 1	as above	Package	180	0
	Control dyeing for No. 2		Package	60	4–5
3	Du Pont Neutral Brown BGL	0.70			
	Du Pont Milling Yellow 5G, Conc.	0.125	Draw ratio	50	0–1
	Du Pont Alizarin Blue Black B	0.125			
	Control dyeing for No. 3		Draw ratio	60	4–5
4	Same as No. 3	as above	Package	50	1
	Control dyeing for No. 4		Package	60	4–5
5	Du Pont Milling Yellow 5G, Conc.	0.54			
	Du Pont Anthraquinone Green G	0.12	Draw ratio	65	1
	Du Pont Anthraquinone Violet R	0.34			
	Control dyeing for No. 5		Draw ratio	30	2–3

* See footnote (‡) to Table I.

junction was added, and the temperature was slowly increased to 85°–90°C as the nylon was thoroughly agitated. Dyeing was continued for 1 hr. at this temperature.

The amount of inorganic salt necessary for forming the sparingly soluble dye salt was found to vary with the nature of the precipitant and the dye. When lead acetate was used, 0.2 g. was sufficient for the dyes investigated. With barium or calcium chlorides, at least 2 g. was required; with some dyes, as much as 20 g. was necessary in order to obtain good equalization.

The results obtained are given in Table III. Outstanding improvements in equalization of color with either draw-ratio or package junctions were obtained with a number of acid dyes and acid-dye mixtures.

TABLE III. NYLON JUNCTIONS DYED WITH SPARINGLY SOLUBLE SALTS

No.	Dye	Salt used to precipitate dye	Amount of precipitant (%, based on nylon wt.)	Junction type	Junction rating*
1	0.5% Du Pont Anthraquinone Green GN	$BaCl_2$	100	Draw ratio	1
	Control for No. 1	—	—	Draw ratio	2–3
2	0.5% Pontacyl Fast Blue GB	$BaCl_2$	100	Draw ratio	0
	Control for No. 2	—	—	Draw ratio	2
3	0.5% "Chromacyl" Black W	$BaCl_2$	1000	Draw ratio	0
4	Same as No. 3	$BaCl_2$	100	Draw ratio	2–3
	Control for Nos. 3 and 4	—	—	Draw ratio	4
5	0.5% "Chromacyl" Black W	$BaCl_2$	1000	Package	0
	Control for No. 5	—	—	Package	5
6	0.5% "Chromacyl" Black W	$CaCl_2$	1000	Package	0
	Control for No. 6	—	—	Package	5
7	0.22% Du Pont Neutral Brown 2RS 0.12% Du Pont Neutral Yeliow GS 0.035% Pontacyl Fast Black N2B, Conc. 200%	$BaCl_2$	500	Draw ratio	0–1
8	Same as No. 7	$BaCl_2$	100	Draw ratio	0–1
	Control for Nos. 7 and 8	—	—	Draw ratio	4
9	Same as No. 7	$BaCl_2$	500	Package	0
10	Same as No. 7	$BaCl_2$	100	Package	0
11	Same as No. 7	$BaCl_2$	50	Package	2
	Control for Nos. 9, 10, and 11	—	—	Package	4–5
12	0.7% Du Pont Neutral Brown BGL 0.125% Du Pont Milling Yellow 5G, Conc. 0.125% Du Pont Alizarin Blue Black B	$BaCl_2$	500	Draw ratio	0–1
	Control for No. 12	—	—	Draw ratio	4
13	Same as No. 12	$BaCl_2$	500	Package	0
	Control for No. 13	—	—	Package	4
14	1.32% Du Pont Neutral Brown BGL 0.14% Du Pont Milling Yellow 5G, Conc. 0.02% Pontacyl Fast Red AS	$Pb(OAc)_2$	10	Package	1–2
15	Same as No. 14	$Pb(OAc)_2$	5	Package	0–1
16	Same as No. 14	$Pb(OAc)_2$	2.5	Package	1–2
	Control for Nos. 14, 15, and 16	—	—	Package	4

* See footnote (‡) to Table I.

In every case differences in dye depth were either eliminated entirely or reduced to very low levels.

A sample dyed by the above procedure was analyzed for barium content for comparison with an uncolored sample treated in exactly the same manner. The dyed sample contained 0.010% of barium, as compared to 0.009% for the undyed sample. The amount of dye on the fiber was of the order of 1%. If color were present as a barium salt, the barium content would have been of the order of 0.10%. Since the amount of barium present was the same in both cases, and too low for the dye to be on the fabric as a barium salt, it is concluded that the color on the nylon was due to sorption of the acid-dye anion and not the undissociated barium dye-salt molecule.

Discussion

A simple explanation of the uniformity of coloration observed in all procedures described is that the concentration of dyes is so low that lodgment on the surface, rather than penetration into the fiber, is the rate-controlling step; conventional dyeing from a relatively concentrated bath assures surface saturation and makes diffusion from the surface to the interior of the fibers the rate-controlling step. Under the dilute bath conditions used in the present tests, diffusion into the fibers keeps the surfaces virtually free of dye. In these circumstances the reverse reaction of desorption appears to be insignificant, and the location of dye molecules becomes a matter of chance. Accordingly, it is concluded that conditions that are favorable to sorption relative to desorption counteract the natural tendency of dye to reside finally in the more amorphous regions or in those regions containing the highest concentration of amine end-groups on the fiber surface.

As mentioned earlier, the necessary conditions for equalizing acid dyes on nylon yarns have been found to be the use of dye baths in which the dye is so dilute as to be colorless to the eye. In such dye baths, uniform dyeing was obtained with nylon sections which had been prepared from yarns designed to show a very sharp differences in shade depth when dyed by the conventional procedure. Even though very little dye is present at any one time, dyeing can be done as rapidly by this method as by conventional procedures by supplying dye to the bath as rapidly as it is removed by the nylon.

Stirring is a very important requirement imposed by this pure-chance mechanism. Unless agitation of the fiber is very efficient throughout the dyeing, spots and lines will be evident at points where the material was gathered or creased. Although such agitation can be obtained easily with small dyeings in the laboratory, increasing difficulty is experienced as the amount of material per dyeing is increased. This is an obstacle to the application of the dilute dye-bath principle to large-scale commercial dyeing using equipment designed for conventional dyeing.

Summary

It has been found that equalization of acid dyes on nylon yarns differing widely in dyeing properties can be obtained by using conditions that are unfavorable for attainment of equilibrium.For this purpose, systems by which dye is supplied to the fiber at a rate below that at which it is sorbed were found effective. Three such systems were investigated: application of the color to the nylon by transfer from wool; controlled mechanical addition of dye to a visually colorless dye bath; and use of the dye in the form of a slightly soluble heavy-metal salt.

Literature Cited

1. McGrew, F. C., and Schneider, A. K., *J. Am. Chem. Soc.* **72**, 2547–52 (1950).
2. McGrew, F. C., and Sharkey, W. H., U. S. Patent 2,459,831 (to E. I. du Pont de Nemours and Co.) (Jan. 25, 1949).
3. Peters, R. H., *J. Soc. Dyers Colourists* **61**, 95 (1945).
4. Sharkey, W. H., U. S. Patent 2,499,787 (to E. I. du Pont de Nemours and Co.) (Mar. 7, 1950).
5. Valko, E. J., Physical Chemistry of Dyeing (chap. 20), in "Colloid Chemistry," Vol. VI (J. Alexander, editor), New York, Reinhold Publishing Corp., 1946.

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Microscopical Observations on the Contents of the Cotton Fiber Lumen*

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Abstract

A method is described for isolating the lumen contents of the cotton fiber by digestion of the cellulose in chilled 72% sulfuric acid. Microscopical observations on the isolated "lumens" as well as the lumen in the whole fiber are reported. The isolated lumens appeared tubular in shape, and electron micrographs of thin sheets of the membrane material showed an unoriented, granular structure.

The lumen residue isolated by sulfuric acid was found to be completely hydrolyzed by 1% sodium hydroxide, but only partly hydrolyzed in dilute mineral acid. Amino acid determination by paper chromatography disclosed no free amino acids in the lumen material; but in an acid-hydrolyzed sample, glutamic and aspartic acids, valine, alanine, and probably serine and arginine were found, in addition to several unidentified amino acids.

IN the microscopical identification of textile fibers, it is of empirical significance that the lumens of different fibers assume characteristic appearances when the fibers are swelled in cellulose solvents. The fluted pattern of the hemp lumen, as opposed to the vermiform lumen in flax, is used as a criterion of distinction, and the lumen shapes in cotton and ramie are equally characteristic; but whether these shapes are a reflection of fundamental structure in a protoplasmic membrane, or only that of the innermost layer of cellulose against which the protoplasm has dried, remains a disputed question.

In the literature on the cotton fiber itself, the lumen is referred to, on the one hand [12], as a cell cavity containing the structureless, desiccated remains of the protoplasm, and, on the other hand [1, 5, 8, 9], as an integral part of the fiber, consisting of a wall or membrane surrounding the cell substance.

The term "lumen" is used in the present report to describe the entire tubular space within the internal boundary of cellulosic walls of the cotton fiber. This work was undertaken to isolate the lumen material of the cotton fiber for the purpose of studying its microscopical form and chemical nature.

In the voluminous literature on the protoplasm of plant cells in general there is repeated justification for a lumen wall separate and distinct from the lumen contents. The "plasma lemma" of Plowe [14], and the "plasma membrane" of Chambers [2], Child [3], Miller [10], and Norris [11] support the concept of a semipermeable wall external to the more liquid phase of the cytoplasm and adjacent to the extraneous coats of the cell wall. Seifriz [17, 18] and Scarth [16] further elaborated the supposition by discussions of orientation in the outer layer of protoplasm, which imply a state of fibrillation of the protein material at the outermost periphery of the cytoplasmic mass. Osterhout [13] concluded that these surfaces consist of nonaqueous films forming boundaries of a layer of aqueous protoplasm not over 10 μ in thickness. In 1943 Serra [19] proposed a theory as to the structure of cytoplasm in which protein layers are made up of polypeptide chains held in place mainly by amide-carboxyl linkages, between layers of which are more or less stable connections by lateral chains, and he explained the semipermeability of the plasma membrane on this basis.

In the work described herein, microscopical examination of the fragments of lumen contents obtained from dried fibers showed the material to be in the form of a flattened tube, while electron micrographs of thin sheets of the material showed it to be granular and unoriented, in opposition to the concept of a fibrillate or organized membrane structure. Microchemical tests confirmed its proteinaceous character.

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Materials and Methods

For microscopical observations of young cotton fibers, samples from bolls of 8 days to 28 days of age were examined in the living condition in isotonic solutions; similar samples were examined after preservation in the usual formalin-alcohol-acetic acid fixative.

For preliminary microscopical examination of the lumen in the whole fiber, samples of commercial cotton were used. Fibers were examined under the microscope at various magnifications while being swelled with several different cellulose swelling agents, such as 72% sulfuric acid, cuprammonium hydroxide, and cupriethylenediamine hydroxide; the staining characteristics and shape of the lumen material were studied under these conditions. Stains used were osmic acid, picric acid, eosin, iodine, ruthenium red, methylene blue, and erythrosin. Micromanipulator needles were used to tease out the lumen contents from the swollen fibers, thus revealing them to exist as a separate entity from the surrounding cellulose wall.

The proteinaceous character of the lumen material was investigated by treating fibers with the xanthoproteic, ninhydrin, Liebermann, and Hopkins-Cole tests. Also, evidence of protein was sought by incubating fibers for a period of 217 hrs. at 35°–40°C in a solution of bacto-trypsin buffered with sodium carbonate to a pH of 8–9; the fibers were removed, washed, and examined microscopically with the various stains. Similar samples were incubated for 143 hrs. at 52°C with papain buffered to pH 6 with potassium acid phthalate and sodium phosphate.

For study of the lumen material separated from the rest of the fiber, a sample of Upland cotton with a high percentage of immature fibers was used in preference to a more highly developed cotton in order that the proportion of cellulose to lumen material would be conveniently low.

The cotton was cleaned as thoroughly as possible by repeated processing through the Shirley analyzer, and the remaining leaf and seed particles were removed by hand with combs and tweezers. It was then dewaxed by Soxhlet extraction with 95% ethyl alcohol for approximately 24 hrs. The pectinaceous material was removed by extracting the dewaxed cotton with 0.5% ammonium oxalate [20] on a water bath for 21 hrs., the oxalate being changed every hour. The sample was then thoroughly washed with distilled water and allowed to dry. The Shirley analyzer was used to untangle the cleaned cotton, and it was subsequently hand-carded to open it up for contact with reagents.

Isolating the Lumen Material with Sulfuric Acid

In order to isolate the lumen material from the rest of the fiber without disturbing its morphological shape, a special technique was developed, based on microscopical observations of the cotton fiber in strong sulfuric acid. A 50-g. sample of the dewaxed and depectinized cotton was covered with a volume of chilled (8°C) 8*M* sulfuric acid sufficient to wet it. After the cotton was completely wetted, the acid was decanted and 2,500 ml. of chilled 12*M* sulfuric acid was added slowly to the cotton and agitated for ½ hr. with an electric stirrer. The mixture was then centrifuged until a good separation of the acid and the degraded cotton was obtained; this required approximately 1 to 1½ hrs. at 900 *G*. The residue, containing swollen fiber fragments and lumen material, rose to the top of the acid and was removed by skimming the surface of the liquid. To this residue, 1,500 ml. of chilled 12*M* sulfuric acid was added; the mixture was agitated for 15 min. and centrifuged until the residue could be removed from the top of the acid with a pipet. This was followed by eight successive treatments of 500 ml. each of chilled 12*M* sulfuric acid. To the final residue, approximately 3 volumes of distilled water were added, an ice bath being used to prevent any rise in temperature. The lumen material was filtered on a frittered-glass filter and washed with distilled water until neutral to litmus. Some of the material was then removed in the wet state for microscopical examination. The residue was dried over calcium chloride before analysis. Because much material was lost by physical manipulation during preparation of the sample, it is not possible to make a quantitative estimate of the amount of lumen material in the fiber, except that it is of the order of less than 0.5%.

Cellulose determinations were made by the polarimetric test of Reeves [15]. Tests for nitrogen in the sulfuric acid centrifugate were made by macro-Kjeldahl determinations, and in the lumen residue by the micro-Dumas method. Amino acids were identified by paper chromatography [4], and carbon, hydrogen, and ash determinations were made by the standard techniques of microchemistry.

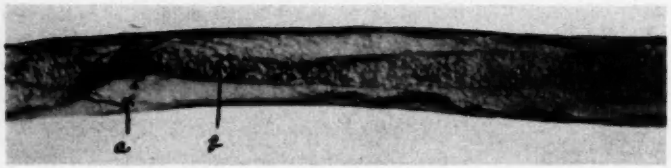


FIG. 1. *Young fiber from unopened cotton boll, fixed in alcohol-acetic acid and stained with methylene blue to show location of lumen. (Magnification, 500 ×.)* a—*Cellulose cell wall.* b—*Lumen.*

Microscopical Examination of the Isolated Lumen Material

In order to determine whether or not the lumen material, as isolated from the fiber, might be a tube rather than a flat sheet, cross sections of the isolated specimens were made for microscopical examination. A drop of undried lumen residue was stained in aqueous safranin for 72 hrs., and was washed on the slide. A single specimen was then embedded in a smear of polyvinyl alcohol between two pieces of contrastingly colored silk, used as markers to facilitate location of the lumen after sectioning. Upon hardening, the film of polyvinyl alcohol containing the lumen fragment and the silk filaments was peeled from the slide, packed in the slot of the Hardy sectioning device [7], and cross-sectioned with a razor blade.

Staining and Shadowing for Electron Microscopy

For examination in the electron microscope, thin sheets of the lumen fragments selected under the wide-field microscope were mounted on the electron microscope screens, and were then shadowed with metallic gold at an angle of approximately 15° [21]. Other specimens were stained with phosphotungstic acid according to the technique of Hall, Jackus, and Schmitt [6].

Results and Discussion

Microscopy of Lumens in the Whole Fiber

In extremely young cells still fresh from the living, growing cotton boll, no lumen boundary could be discerned microscopically, and the contents consisted of a fine granular mass, without apparent continuity. In a few observations on living mature fibers, there was some indication of a boundary, but it could not be detected by staining as distinctly as could the granular lumen contents at the center. No clear evidence was obtained in these investigations for a lumen membrane in the living cell; it is only after plasmolysis due to natural death and desiccation, or to artificial killing with such fixatives as alcohol and formalin (Figure 1), that the protoplasm in the cotton fiber lumen manifests a solid membrane as a boundary.

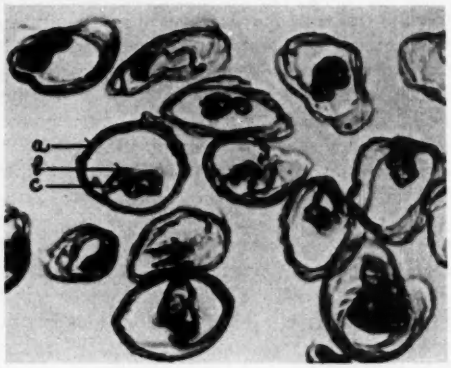


FIG. 2. *Cross sections of young fibers, showing tubular lumens shrunken away from cellulose fiber walls after fixation. (Magnification, 250 ×.)* a—*Cellulose cell wall.* b—*Tubular lumen.* c—*Hollow lumen center.*

The tendency of the lumen material to set in the form of a tube separate from the cellulose cell wall when the fiber dries is confirmed by cross sections of fibers on a very young seed taken from an unopened boll and fixed in the usual preservative solutions (Figure 2).

The center of this lumen tube is sometimes hollow and sometimes filled with fine granules, and although our observations have confirmed the tubular character of the lumen contents in several fibers, they do not preclude the possibility that the material may sometimes occur as a solid mass of coagulated or of granular material, depending upon the conditions of plasmolysis. The presence of a large liquid-filled vacuole, common in a rapidly growing cell such as the cotton fiber, would account for the formation of the plasma membrane in a thin surrounding sheath when the water is lost from the vacuole at maturity and death.

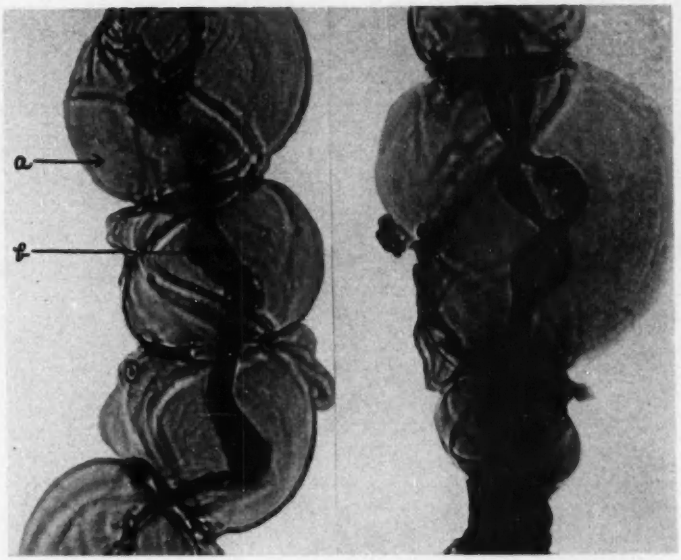


FIG. 3. *Cotton fibers stained with methylene blue and swelled with cuprammonium hydroxide to show lumen as dark-stained, nonswelling mass in center of fiber. (Magnification, 500 ×.)* a—*Swollen cellulose wall.* b—*Tubular lumen.*

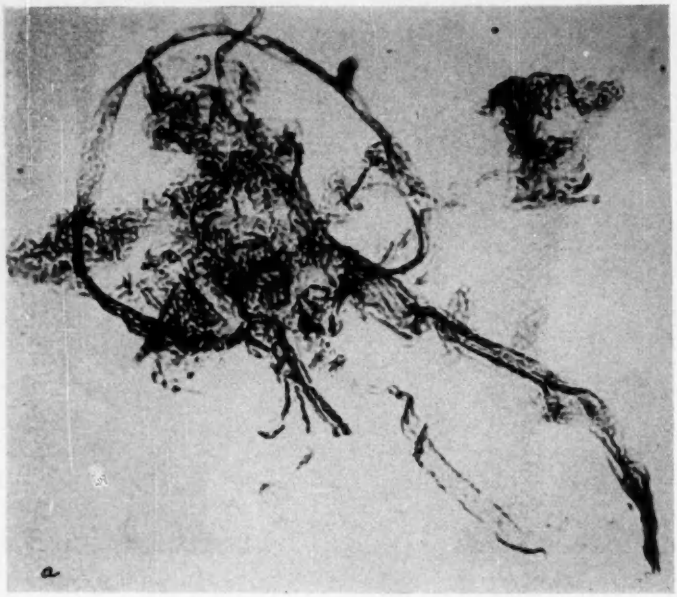
Microscopical observations of fibers from commercial cottons indicated that in the plasmolyzed, desiccated state of the dead cotton hair, the lumen material does actually have a tubular shape, at least for a part of its length. When this lumen material was freed from the fiber, by swelling with cellulose solvents, it often had the crumpled appearance of a collapsed tube (Figure 3).

The noncellulosic nature of this tubular entity was confirmed by its positive staining with selected staining reagents. Chemical tests for protein material—xanthoproteic, ninhydrin, Liebermann, Hopkins-Cole—also gave positive reactions. No change was observed in the microscopical appearance or reactions of the lumen material inside the fiber after extraction of the fibers with water, 95% ethyl alcohol, or dilute salt solution. However, the lumen contents were found to be entirely dissolved from the fiber by dilute alkali, and partially so by dilute hydrochloric or nitric acid. Both trypsin and papain, under proper conditions of digestion, completely removed the lumen material from the cotton fibers.

Microscopy of Isolated "Lumens"

When the washed, but undried, residue of lumen material, isolated from immature cotton fibers by sulfuric acid digestion, was examined, it was found (Figure 4a) to consist mostly of entities with the same shape and appearance as the lumen contents observed inside swollen cotton fibers (Figure 3). In addition, there was considerable granular material associated with the intact lumen fragments, and all of this residue could be stained with any of the several reagents used for staining lumens in the whole fiber. When taken from the residue and cross-sectioned, single specimens (Figure 4b) of the intact lumen material appeared to be flattened, collapsed tubes (Figure 4c), similar in shape to an immature cotton fiber.

Specimens of isolated lumen material examined under the electron microscope after staining with phosphotungstic acid showed no evidence of a fibrillar structure in the protein membrane (Figure 5a). Specimens shadowed with metallic gold (Figure 5b) were similar in appearance to preparations of protoplasm from other plant sources photographed through the electron microscope by other workers [21]. The effect of the conditions of electron microscopy on the specimen should be taken into account in the interpretation of these results, but it is obvious that there is no pattern of fibrils comparable to that found in cellulose membranes.



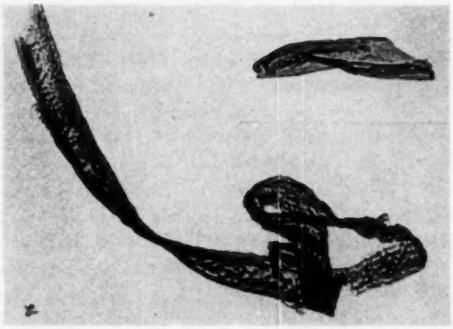


FIG. 4. *Cellulose-free lumen residue from sulfuric acid treatment.* a—*Mass of fragments (magnification, 330 ×).* b—*Isolated individual fragments (magnification, 460 ×).* c—*Cross sections of isolated fragments (magnification, 1700 ×).*

Chemical Analysis

Macro-Kjeldahl analyses on the sulfuric acid centrifugate indicated negligible loss of nitrogen during the sulfuric acid treatment to remove the cellulosic part of the fiber. A test for cellulose content of the dried lumen residue made by the polarimetric method of Reeves [15] showed that after digestion of 12 mg. of the lumen residue with cuprammonium hydroxide, no optical rotation was observed in the solution, whereas under the conditions employed, 0.4 mg. of cellulose would have produced a *levo*-rotation amounting to 0.05°.

Amino acid determination by paper chromatography [4] disclosed no free amino acids in the residue, but in a hydrolyzed sample of the material, spots corresponding to glutamic and aspartic acids, valine, alanine, probably serine and arginine, and other unidentified amino acids were indicated on the chromatogram. Further analysis of the dried residue indicated it to contain:

FIG. 5. *Electron micrographs of fragments of lumen membrane. (Magnification, 17,000 ×.)*
a—*Stained with phosphotungstic acid.* b—*Shadow-cast with gold.*

Nitrogen (total)	4.45%
Hydrogen	5.88%
Carbon	56.55%
Phosphorus	0.11%
Ash	9.67%

Identification of amino acids in the material confirms the assumption that it is of a proteinaceous character; that proteolytic enzymes as well as dilute caustic solutions can completely free the lumen cavity of all solid matter is additional evidence. It is to be assumed that carbohydrates and lipids also occur in the lumen material of the cotton fiber, but no attempt was made in these studies to investigate the classes of compounds.

Summary

1. Microscopical observations on living fibers from young bolls indicated that the protoplasmic membrane in the cotton fiber is not discernible as a discrete and continuous boundary until after coagulation during plasmolysis.

2. The lumen contents of dry cotton hairs can be separated from the rest of the fiber by successive treatments with cold 72% sulfuric acid solution without changing their apparent structure.

3. Individual pieces isolated by the sulfuric acid method and cross-sectioned were found by microscopical observation to have a tubular shape, and electron micrographs of thin sheets of this lumen material revealed a spongy, granular structure without any fibrillar orientation.

4. The lumen material is of a proteinaceous nature—it was completely dissolved from the centers of the fibers by the action of appropriately buffered proteolytic enzymes (trypsin and papain); and, upon acid hydrolysis of the lumen material obtained by the sulfuric acid separation method, amino acids were detected by paper chromatography.

Acknowledgment

The authors wish to express their appreciation to numerous fellow staff members for their helpful counsel and suggestions. Particular thanks are due Dr. Richard E. Reeves for cellulose determinations, Mr. Wilson A. Reeves for amino acid paper chromatographs, and Mr. Lawrence E. Brown for microanalyses. Electron micrographs of the prepared specimens were made by Mr. Nathan O'Neal of Tulane University and Mr. Verne W. Tripp of our staff. Acknowledgment is made to Mr. O'Neal for his work with us on this study, and to Tulane University for its cooperation in making the instrument available to us.

Literature Cited

1. Bailey, T. L. W., Jr., in "Matthews' Textile Fibers," 5th edition (edited by H. R. Mauersberger), New York, John Wiley & Sons, 1947, pp. 198–229.
2. Chambers, R., in "Colloid Chemistry" (edited by J. Alexander), Vol. 5, New York, Reinhold Publishing Corp., 1944, pp. 864–75.

3. Child, C. M., in "Cell and Protoplasm" (edited by F. R. Moulton), New York, Science Press, 1940. (Am. Assoc. Advance. Sci. Pub. No. 14.)
4. Consden, R., Gordon, A. H., and Martin, A. J. P., *Biochem J.* **38**, 224–32 (1944).
5. Denham, H. J., *J. Textile Inst.* **13**, T99 (1922).
6. Hall, C. E., Jakus, M. A., and Schmitt, F. O., *J. Applied Phys.* **16**, 459 (1945).
7. Hardy, J. I., *U. S. Dept. Agr. Circ.* No. 378, Washington, D. C., Govt. Printing Office, 1935.
8. Levine, B. S., *Science* **40**, 906 (1914).
9. Mangenot, C., *Rev. sci.* **81**, 483 (1943).
10. Miller, E. C., "Plant Physiology," 2nd edition, New York, McGraw-Hill, 1938.
11. Norris, C. H., *J. Phys. Chem.* **46**, 1111 (1942).
12. Osborne, G. G., TEXTILE RESEARCH **5**, 292 (1935).
13. Osterhout, W. J. V., *J. Gen. Physiol.* **28**, 343 (1945).
14. Plowe, J. R., *Protoplasma* **12**, 196, 221 (1931).
15. Reeves, R. E., *J. Biol. Chem.* **154**, 49 (1944).
16. Scarth, G. W., in "A Symposium on the Structure of Protoplasm; a Monograph of the American Society of Plant Physiologists" (edited by W. Seifriz), Ames, Ia., Iowa State College Press, 1942, pp. 99–107.
17. Seifriz, W., in "A Symposium on the Structure of Protoplasm; a Monograph of the American Society of Plant Physiologists" (edited by W. Seifriz), Ames, Ia., Iowa State College Press, 1942, pp. 245–64.
18. Seifriz, W., "Protoplasma," New York, McGraw-Hill, 1936.
19. Serra, J. A., *Anais faculdade farm. Porto* **5**, 171 (1943) (through *Biol. Abstracts* **20**, 2151 (1946)).
20. Whistler, R. L., Martin, A. R., and Harris, M., *J. Research Natl. Bur. Standards* **24**, 555 (1940).
21. Wyckoff, R. W. G., "Electron Microscopy; Technique and Applications," New York, Interscience, 1949, pp. 133, 135.

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Some Observations on the Constitution of the Primary Wall of the Cotton Fiber*

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Abstract

The primary wall of fully matured cotton fibers has been isolated and its morphology and composition studied by electron microscopic examination and by chemical analyses. The primary wall appears to contain about 50% cellulose; protein, wax, and pectic substances occur in lesser amounts; cutin or suberin and mineral matter are also present. The concentration of noncellulosic substances in the primary wall is much greater than in the whole fiber.

Electron microscopic examination of the primary wall indicates that it consists of a network of cellulose fibrils, having diameters of 100–400 Å., surrounded by the noncellulosic constituents. The oriented fibrillar systems observed with the polarizing microscope have not been seen in the electron micrographs of the specimens studied. There is an apparent increase in the diameter of the fibrils of the primary wall and in the denseness of the network as the fiber matures. The existence of layers in the cellulose network has been observed.

IN THE DEVELOPMENT of the cotton fiber, the first membrane formed is the only covering of the growing cell until such time as it attains its maximum growth in length and begins to thicken. This membrane, known as the primary wall, persists thoughout the life of the fiber as its outer covering, being present in the commercial fiber used in yarn and fabric manufacture.

The growth history of the cotton fiber consists of a period of cell elongation and a period of wall thickening. On the day of flowering, swellings appear on the outer wall of the epidermal cells of the seed coat.

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These swellings elongate to form tubular outgrowths whose diameters are of the order of 15 μ, and of lengths thousands of times as great, the diameter being reached soon after the fiber originates. During this period of elongation the living protoplast is enclosed only by the thin primary wall. After elongation has virtually ceased, the secondary wall is deposited diurnally in concentric layers from the inner surface of the primary wall toward the center of the fiber.

The technological significance of the primary wall lies in the fact that it is the first, and in some cases the only, morphological component of the cotton fiber to come in physical contact with the processing environment. In the mechanical processing of cotton, that portion of the fiber which is completely embraced by the primary wall has a profound significance on spinnability [15], presumably because of the wax present on the fiber surface. The presence of noncellulosic substances in the primary wall modifies the dyeing properties, rate of reaction, and wettability of the fiber, since in such operations the reagents reach the fiber body by passage through the primary wall. The resistance of the fiber to attack by abrasion and microorganisms is also conditioned by the presence of the primary wall.

The present study was undertaken to extend the fundamental knowledge of the structure of the primary wall of commercial mature cotton fiber, mainly through the technique of electron microscopy, and to determine the chemical composition of the wall. Earlier work on the cell-wall structure of cotton and other plant fibers [1, 2, 3, 7, 8, 12, 13] has provided a fairly complete picture of the primary wall of the cotton fiber as interpreted from observations with the light microscope, but much of the information was gained from studies on the fiber prior to the formation of secondary thickening.

Earlier Work

According to earlier work, the primary wall is a membrane less than 0.5 μ in thickness; it is more resistant to the action of cellulose solvents than is the secondary wall of the fiber; it can be stained deeply with ruthenium red, showing that pectic substances are present; it likewise shows a faint coloration with fat stains like Sudan IV, indicating the presence of wax.

Prior to the development of the secondary wall of the fiber, the primary wall does not give typical cellulose staining reactions without purification; the primary wall of the mature fiber will show the presence of cellulose by these tests, but the colors developed are usually faint. After removal of noncellulosic substances from the mature wall by appropriate extraction, the microchemical tests for cellulose are readily obtained. Sisson [23] has demonstrated that x-ray diffraction patterns of primary-wall material are typical of cellulose.

Although knowledge on the point is very incomplete, it generally has been believed that the noncellulosic substances present in cotton are largely restricted to the primary wall [13], together with the lumen, which contains the desiccated protoplasm of the cell. It has been shown that pectic substances make up about 5% of the fiber weight up to the point where secondary thickening begins [25]. The location of the noncellulosic substances in the primary wall proper—whether dispersed through its thickness or being merely an external coating—has remained a point of conjecture. It has been thought that the wax present in cotton is in the primary wall alone, possibly as a coating on the outside of the wall [20]. The concept of an intimate dispersion of the noncellulosic substances throughout the primary wall has been advanced [12].

Examined microscopically in normal light, neither raw nor purified primary wall shows any definite structure. Between crossed Nicols, raw wall shows virtually no birefringence, and that freed of noncellulose shows only a slight degree. However, if either material is stained with a dichroic dye (Congo red), it exhibits a pronounced network structure which appears to be made up of two systems of interwoven fibrils lying at about 70° inclination to the fiber axis and anastomosing with each other [1, 3, 12]. Anderson and Kerr [1] also indicated the existence of a third system of fibrils oriented perpendicularly to the fiber axis, apparently in the same plane as the other systems.

Electron microscope studies by Muhlethaler [18] showed a felted mass of fibrils randomly oriented in the primary wall, as opposed to closely arranged bundles of parallel fibrils in the secondary wall. This appeared to be equally as typical of ramie and flax as of cotton. The diameter of individual fibrils in either wall was estimated to be between 250 and 400 Å. No attempt has been made to correlate these findings with the pattern of coarser threads or bands observed with the polarizing microscope [1, 12].

Experimental

Muhlethaler [18] has shown that it is possible to separate the primary and secondary walls of plant fibers by beating in water in a Waring Blendor. Figure 1 shows a beaten cotton fiber, stained with ruthenium red, in which some of the primary wall has come free of the fiber body and appears as a sleeve of material in the lower part of the figure. This method of separation had advantages over alternative means in which the wall is partly destroyed or markedly affected, or which demand much tedious manipulation.

In this study, a number of beating media other than water were tried, but none gave results as satisfactory. Beating in carbon tetrachloride did not appear to affect the fibers even after long periods, while extensive beating was required in ethyl alcohol before any fibrillation of the primary wall was noticeable [4]. Salt solutions (10% sodium chloride or sodium bromide) worked as well as pure water, but appeared to affect materially the primary wall separated and were difficult to remove. It appears that some degree of swelling of the fiber is necessary in order to achieve separation of the cell walls by beating.

The isolation of quantities of cell-wall material large enough for quantitative analytical work is made feasible by the fact that the freed primary wall rises to the top of the suspension of beaten fibers, while the secondary wall, with much primary wall still attached, settles. This separation may be enhanced by gentle aeration of the suspension after beating. Attempts to demonstrate a difference in density of the cell-wall materials were not successful.

It was found that about 40 mg. of primary-wall material could be prepared from 15 g. of cotton by the following method:

The cotton, carefully cleaned to remove trash particles, is cut into ½-in. lengths, and is soaked in water for 15 min. Half-gram portions of cotton are then placed in 200 ml. of water in the Waring Blendor and are beaten for 1 min. at high speed. The several lots of beaten cotton are combined in a large beaker, a stream of air is passed through the suspension with gentle stirring for 10 min., and the suspension is allowed to stand for another 10 min. All but 300 ml. of the suspension is decanted, the decanted portion is put through the process of aeration, and the top liter is decanted. The decanted liter, which is now largely free of secondary wall, is centrifuged. The cell-wall material concentrates at the bottom of the centrifuge tubes. The slurry of cell-wall material is passed through an 80-mesh stainless-steel screen, which allows most of the primary-wall fragments to pass while retaining the larger secondary-wall pieces. Observation of the material obtained between crossed

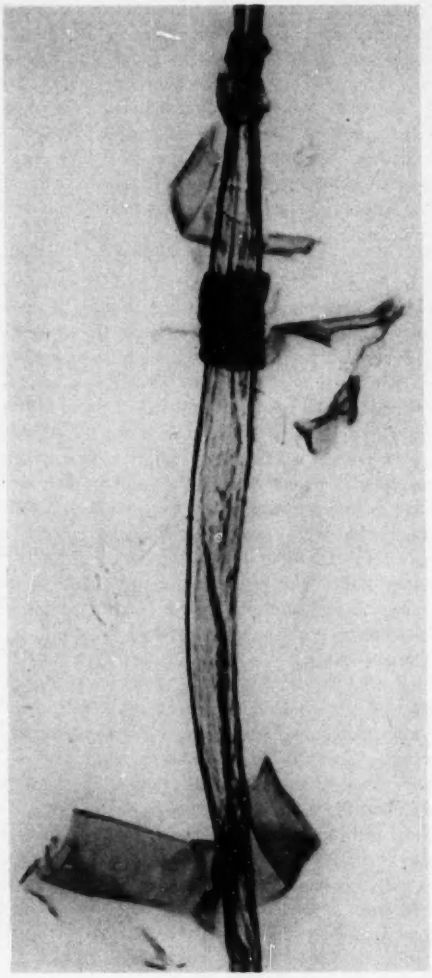

FIG. 1. *Cotton fiber, beaten in water in the Waring Blendor and stained with ruthenium red, showing primary wall coming free of the fiber body. Magnification, 500 ×.*

Nicols will indicate the presence of secondary-wall particles, which are brilliantly birefringent. After passage through the sieve, virtually no birefringent material can be detected in the cell-wall material. Extension of the time of beating in the Waring Blendor produces fibrillation of the secondary wall, making isolation of the primary wall more difficult.

The primary-wall material prepared in this manner retained the form of unruffled sheets or sleeves if kept wet with water, but shriveled, shrank, and rolled up if allowed to dry. Rewetting did not cause a return to the original wet appearance.

Chemical analyses were made on the primary-wall material after drying to constant weight in a vacuum oven at 45°–50°C and 100 mm. pressure into which entered a slow stream of air dried by passage through sulfuric acid. Amounts of material taken for analysis ranged from 10 to 20 mg., and duplicate or triplicate determinations were made except where noted. The data reported are those obtained on the primary wall of cotton of the Empire variety.

Alcohol-soluble material in the primary wall was determined by repeated extraction with hot (60°C) 95% ethyl alcohol [6]. The sample was held in a sintered glass crucible, and extraction was continued until no weight loss occurred on successive extractions. The alcohol was drawn off and renewed at 10-min. intervals. The total extraction time was about 1 hr. The alcohol-soluble matter amounted to 7.6%. It is assumed that the extractible material consists largely of the complex mixture of waxes, fatty acids, hydrocarbons, etc., which make up cotton wax [10].

Pectic substance was determined as anhydrogalacturonic acid by the method of Stark [24]. The primary-wall material contained 8.8% pectic substance. It was noted that the material on which this determination had been carried out still stained slightly with ruthenium red, an indication that small amounts of pectic material or protein remained, or that oxycellulose was present in the material.

The nitrogen content of the wall ranged from 1.9% to 2.8% by the Dumas method. Since water-soluble nitrogenous compounds would have been removed previously in the beating and wetting treatments, it is likely that this nitrogen was present as protein or possibly as chitin or aminocellulose. No glucosamine was detected in the acid hydrolyzate of the primary wall, using the color test described by Morgan and Elson [17], which gave positive results with minute amounts of a known sample of chitin. The staining reactions for proteins, however, did not show well-defined results on the primary wall. Prior to acid hydrolysis, no amino acids could be detected by paper chromatography; after hydrolysis, the presence of serine, aspartic acid, glycine, and two other unidentified amino acids was indicated by this technique. The average percentage of nitrogen found in the primary wall multiplied by 6.25 to convert to protein gives a protein content of 13.8%.

The cellulose content of the primary wall was estimated in two ways. The first of these was to digest the alcohol-extracted material with monoethanolamine [22] for 3 hrs. at 150°C, washing free of the reagent, and drying to constant weight. The residue after this extraction averaged 58% of the original raw sample. Subsequent treatment of this residue with cuprammonium hydroxide solution for a period of 16 hrs. left 3.5% of insoluble matter. The ethanolamine-extracted residue gave no staining reaction with ruthenium red, indicating the effective removal of pectic substances and presumably protein. On the assumption that this residue contained only cellulose and cuprammonium-insoluble material, the cellulose content of the wall would appear to be about 54%.

The second way in which cellulose was estimated was to measure the optical rotation of cuprammonium hydroxide dispersions of primary-wall material by the method of Reeves [21]. By this method, the raw primary wall contained 46% cellulose, the alcohol- and ethanolamine-extracted material about 60%–70% (single observations). A reducing-sugar determination on the completely hydrolyzed raw primary-wall material gave a result of 49% as glucose.

The 3.5% of material remaining after alcohol, ethanolamine, and cuprammonium hydroxide extractions had the staining reactions and general chemical behavior characteristic of cutin or suberin [11].

The residue remaining after ashing raw primary wall was approximately 3% of the weight of the dry starting material. Spectrographic analysis demonstrated the presence of aluminum, calcium, copper, iron, magnesium, manganese, and silicon. Cobalt, potassium, and phosphorus were completely absent, and sodium was present only in spectroscopic-trace quantities.

Electron microscopic examinations were made with an R.C.A. EMU instrument (zero-bias gun). Specimens of the primary wall were mounted on specimen

FIG. 2. *Pieces of purified primary wall of mature cotton fiber, stained with Congo red and photographed between crossed polaroids. Magnification, 1150 ×.*

grids without supporting membrane, as the fragments were large enough to support themselves. When it was desired to examine extracted material, extractions were carried out with the specimen mounted on the grid; this was found to be a relatively easy way to prepare mounts of extracted material, which is more difficult to handle than raw primary wall. Gold or chromium shadowing was used on most of the specimens observed. Polystyrene latex particles (2,800 Å. in diameter) were employed as reference objects for purposes of calibration.

Structure of the Primary Wall

The primary wall shows no structural detail by microscopic examination in unpolarized light even after removal of noncellulosic constituents and staining with cellulose stains. Between crossed polaroids, the raw wall is very slightly birefringent, and this property is enhanced to some extent after purification by alcohol extraction and digestion with ethanolamine. Stained with Congo red, the purified wall shows a rather vague criss-cross or network structure between crossed polaroids (Figure 2). Hock, Ramsay, and Harris [12] and Anderson and Kerr [1] have shown this pattern in young fibers having no secondary-wall growth. The width of the bands or fibrils forming the network is of the order of 1 μ. The orientation of the bands in directions making an angle of some 70° with the fiber axis is apparent.

Figures 3 and 4 are electron micrographs showing the appearance of the raw primary wall of a young fiber and that of a mature fiber, respectively. The transparency of the primary wall to the electron beam as shown by these and subsequent figures indicates that the thickness of the wall is considerably less than 0.5 μ, and probably less than 0.2 μ. In these pictures the wall seems to consist mostly of material which has no recognizable structure at these magnifications, although the underlying cellulose structure is faintly discernible in the young fiber wall.

Removal of the alcohol-soluble material in the primary wall allows the underlying structure to be seen more clearly, although a considerable amount of matter masks the main cellulose structure. Figure 5, which shows the appearance of alcohol-extracted primary wall of mature Empire fiber, indicates that the wax was present between the fibrils of the cellulose network. The fibrils and remaining noncellulosic substances form a coherent membrane in which the noncellulosic material is intimately distributed in the interstices of the network.

After digestion of the alcohol-extracted wall with ethanolamine, the electron microscope reveals a fine

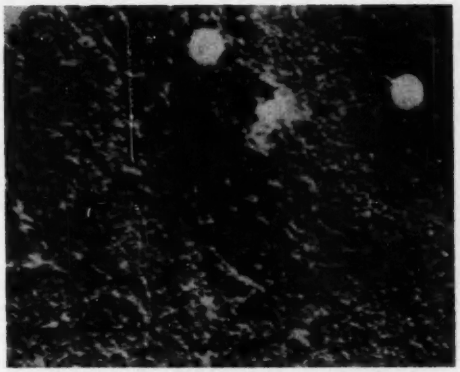

FIG. 3. *Raw primary wall of 8-day-old Rowden cotton fiber. Spheres are polystyrene latex particles. Gold-shadowed.*

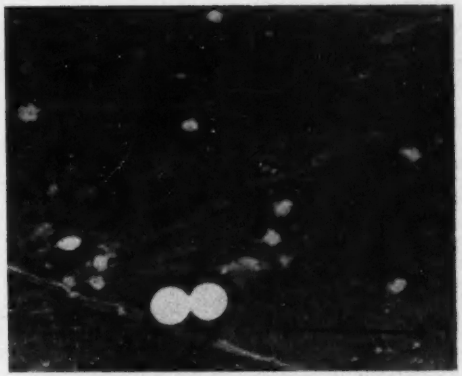

FIG. 4. *Raw primary wall of mature Empire cotton fiber. Gold-shadowed.*

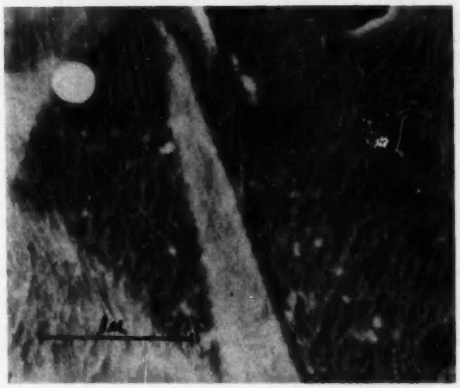

FIG. 5. *Alcohol-extracted primary wall of mature Empire cotton. Gold-shadowed.*

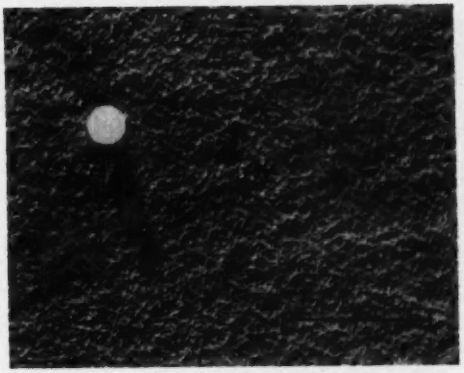

FIG. 6. *Purified primary wall of 8-day-old Rowden cotton fiber. Gold-shadowed.*

woven network of fibrils which are undoubtedly the major constituent of the wall. Figure 6 shows the cellulose network of a purified young (8-day-old) Rowden fiber wall. It is seen that the fine structure is already highly developed at this stage of growth. The primary-wall cellulose structure of a mature Rowden fiber grown in the same field as the fiber of Figure 6 is shown in Figure 7. A comparison of the walls at the two stages of growth indicates that the older wall possesses a more densely felted appearance, and that the average diameter of the fibrils of the older wall is greater. It is not possible to put an upper limit on the length of the fibrils because of the interwoven texture of the structure. The diameter of the fibrils appears to range from 100 to 250 Å. in both specimens shown. Fibrils wider than these appear to be present in the primary wall of mature Empire cotton (shown in Figure 8). In this specimen, the average fibril diameter is greater than in either specimen of the Rowden wall, many of the fibrils appearing to be more than 400 Å. wide. The measurement of fibril diameter is complicated by the presence of shadowing metal in layers 20 to 60 Å. thick.

Occurrence of layers in the cellulose network is frequent. In Figure 9 an area of the wall of a

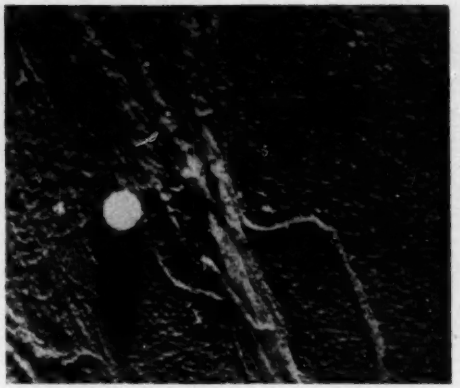

FIG. 7. *Purified primary wall of mature Rowden cotton fiber grown in the same field as the fiber of Figure 6. Gold-shadowed.*

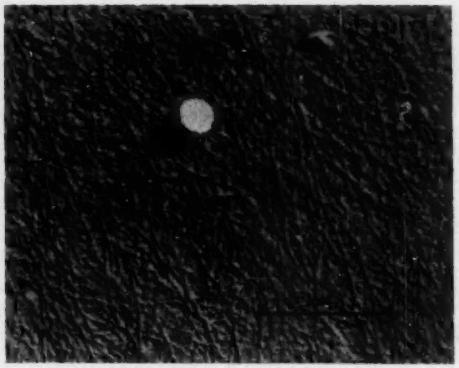

FIG. 8. *Purified primary wall of mature Empire cotton fiber. Chromium-shadowed.*

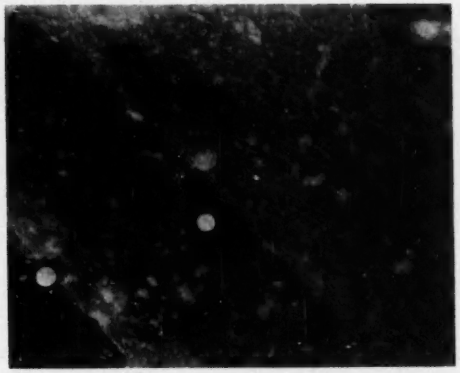

FIG. 9. *Purified 3-day-old Rowden fiber, showing layers in cellulose network of primary wall. Gold-shadowed.*

3-day-old Rowden fiber shows at least three such layers. Mature primary wall also displayed this characteristic. It is unlikely that the sharp boundaries defining the layered regions are artifacts introduced during specimen preparation. Occasionally, regions resembling the pit formations demonstrated by Muhlethaler [19] in meristematic cells were observed in primary-wall material after extraction procedures with dilute sodium hydroxide and alcohol. The presence of noncellulosic material in the immediate vicinity of these points was evident.

Discussion

The description of the primary wall of the cotton fiber on the basis of the observations made in this study both with the light and with the electron microscope is in general agreement with that of previous workers who have studied fibers prior to secondary growth.

The organized fine structure of the primary wall as revealed by electron microscopy extends to dimensions much smaller than those indicated by light microscopy, but in the specimens studied close correlation of the details of the wall structure as indicated by both methods is not apparent. This lack of correlation appears in a consideration of the orientation of the cellulose structure of the wall. Light photomicrographs of the primary wall after removal of noncellulosic material, such as those of Hock, Ramsay, and Harris [12] and Figure 2, indicate orientation of the structure at an angle of about 70° to the fiber axis. With the electron microscope, it appears that such orientation does not extend to the level of the cellulosic fibrils making up the wall. The width of the oriented structural members appearing in the light photomicrographs is of the order of 1 μ. No corresponding entity of these dimensions is seen in the electron micrographs, even when orientation is not a consideration.

In the work reported here, it was not possible to mount specimens in the electron microscope in such a way that the fiber axis was known. The specimens studied appeared to have a random arrangement

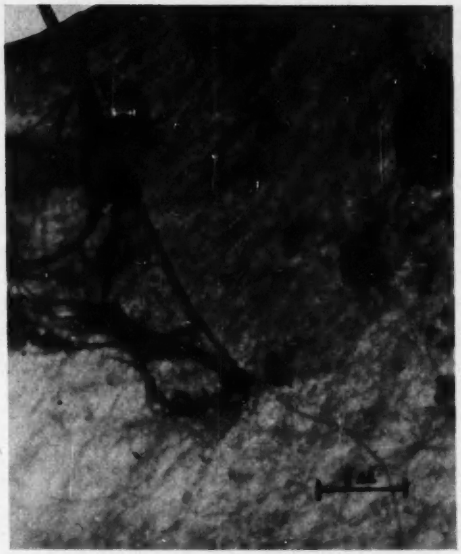

FIG. 10. *Unshadowed purified primary wall (positive print).*

of the fibrillar structure. Emphasis on one direction or another in the photographs seems to be the result of the shadow-casting process, by which the fibrils running in a direction normal to the direction of shadowing are accentuated. Figure 10 shows the appearance of purified mature primary wall without metal shadowing. Here, as in the shadowed specimens, no marked orientation of the fibrils is apparent. However, the possibility of an "over-all" orientation of the fibrils in the directions of the systems indicated by observation with the polarizing microscope cannot be ruled out.

Examination of unshadowed primary wall after purification shows the existence of regions of varying thickness, as judged by difference in transparency to the electron beam. The width of these regions is of the order of several microns, and they are of an indeterminate length. Often they have the aspect of folds or ruffles in the wall. Bailey [2] points out that the structural patterns seen in the primary walls of wood, etc., are due to inequalities of thickness of the cell wall. The existence of layers such as those shown in Figure 9, as opposed to folds, in the primary wall is another possible explanation for the

TABLE I. CHEMICAL COMPOSITION OF TYPICAL COTTON FIBER * AND PRIMARY WALL

Constituent	Percent of dry weight†	
	Fiber	Primary wall
Cellulose	94	54
Protein (% N × 6.25)	1.3	14
Pectic substance	1.2	9
Wax (alcohol-solubles)	0.6	8
Ash	1.2	3
Cutin/suberin(?)	—	4

* From U. S. Dept. Agriculture Publication AIC-61 [10].
† Moisture regain of fiber, 8%; of primary wall, 13%.

banded appearance of the wall observed between crossed polarizers.

Increase of the diameter of fibrils constituting the primary wall during the growth period is in line with the observations of Muhlethaler [19] on maize coleoptiles. The finer fibrils appear to fill in the spaces between the larger fibrils, producing a densely felted fibrillar texture.

The well-defined network structure of the cellulose of the primary wall is in striking contrast to the highly parallelized fibrillar arrangement of the secondary wall of cotton [14, 18]. The observed fibril diameters are approximately the same in both walls in the mature fiber (100–400 Å.), although subfibrils of 60 Å. diameter have been reported in cellulose fibers beaten ultrasonically [9]. These subfibrils were probably of secondary-wall origin.

The chemical composition of the primary wall of the cotton fiber is qualitatively similar to that of the whole fiber, but the concentration of noncellulosic constituents is much higher in the primary wall. In Table I is presented a comparison of the chemical composition of typical cotton (whole fiber) [10] and the primary wall of the Empire cotton used in this study.

The contribution of the primary wall to the total weight of the cotton fiber may be estimated in an approximate manner from geometric considerations, assuming the density of the primary and secondary walls to be the same. Taking a fiber of circular cross-sectional area of 120 square microns, the primary wall of 0.2 μ thickness would be about 5.7% of the total fiber weight; if the wall were 0.1 μ thick, it would amount to 2.5% of the fiber. If the fiber has a cross section of elliptical shape, the contribution of the primary wall to total fiber weight is somewhat greater, as calculated in this manner.

The belief that the wax of the cotton fiber is located

principally, if not exclusively, in the primary wall of the fiber [16] seems to be borne out from a consideration of the wax (alcohol-solubles) content of the primary wall. If the primary wall is 5% or more of the fiber, the wax content of the primary wall alone is at least 0.4% of the fiber weight, a large fraction of the wax content of the typical fiber. A determination of the wax content by the Conrad method [6] on the Empire cotton used in these experiments before and after removal of some of the primary wall by beating in water showed a decrease from 0.75% to 0.65%. This relatively large change in the wax content of the fiber by removal of a small portion of the fiber wall also indicates that the majority of the wax is present in the primary wall, or near to the surface of the fiber.

Proteinaceous matter in the fiber would appear to be distributed in the primary wall and in the lumen. In a study of the lumen material of the cotton fiber [5], it was estimated that this material amounted to as much as 0.5% of the fiber, and it was shown that it was largely proteinaceous. Assuming the primary wall to be 5% of the fiber and to contain 14% protein, the sum of the protein contents of primary wall and lumen approaches the total protein content of the typical fiber (Table I).

The pectic substance present in the primary wall apparently does not account for the total pectic content of the fiber. The primary wall would have to be some 13% of the fiber to enable us to conclude that the pectic material was restricted to the primary wall.

The ash content found for primary wall beaten off in water probably does not correspond to the value for the wall in its original state. The absence of potassium and the small quantity of sodium found in the ash are at variance with the ash composition of typical fibers [10], in which both of these elements are present in relatively large quantities. The small amounts indicated by spectrographic analysis lead to the conclusion that the sodium and potassium salts were leached out of the wall during the beating process.

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Appreciation is expressed to members of the Analytical and Physical Division and to Dr. R. E. Reeves of the Cotton Fiber Division of the Southern Regional Research Laboratory for some of the analytical data reported in this paper. The authors are also grateful to C. W. Daniels of Charity Hospital, New Orleans, La., Electron Microscope Laboratory, who materially aided in the progress of this work, and to Charity Hospital and Tulane University Biophysics Department, through whose courtesy the electron microscope was used.

Literature Cited

1. Anderson, D. B., and Kerr, T., *Ind. Eng. Chem.* **30**, 48 (1938).
2. Bailey, I. W., *Ind. Eng. Chem.* **30**, 40 (1938).
3. Balls, W. L., *Proc. Roy. Soc. (London)* **B95**, 72 (1923).
4. Barnes, R. B., and Burton, C. J., *Ind. Eng. Chem.* **35**, 120 (1943).
5. Catlett, M. S., Giuffria, R., Moore, A. T., and Rollins, M. L., TEXTILE RESEARCH JOURNAL **21**, 880 (1951) (this issue).
6. Conrad, C. M., *Ind. Eng. Chem., Anal Ed.* **16**, 745 (1944).
7. Frey-Wyssling, A., "Submicroscopic Morphology of Protoplasm and Its Derivatives," New York, Elsevier Publishing Co., 1948.
8. Frey-Wyssling, A., *Ann. Rev. Plant Physiol.* **1**, 169 (1950).
9. Frey-Wyssling, A., and Muhlethaler, K., TEXTILE RESEARCH JOURNAL **17**, 32 (1947).
10. Guthrie, J. D., Hoffpauir, C. L., Steiner, E. T., and Stansbury, M. F., "Survey of the Chemical Composition of Cotton Fibers, Cottonseed, Peanuts, and Sweetpotatoes; A Literature Review," U. S. Dept. Agriculture Publication AIC-61 (Revised), 1944.
11. Haas, P., and Hill, T. G., "An Introduction to the Chemistry of Plant Products," Vol. I, London, Longmans, Green and Co., 1928.
12. Hock, C. W., Ramsay, R. C., and Harris, M., *J. Research Natl. Bur. Standards* **26**, 93 (1941).
13. Kerr, T., TEXTILE RESEARCH JOURNAL **16**, 249 (1946).
14. Kinsinger, W. G., and Hock, C. W., *Ind. Eng. Chem.* **40**, 1711 (1948).
15. Knecht, E., *J. Textile Inst.* **2**, 22 (1911).
16. Marsh, P. B., Barker, H. D., Kerr, T., and Butler, M. L., TEXTILE RESEARCH JOURNAL **20**, 288 (1950).
17. Morgan, W. T. J., and Elson, L. A., *Biochem. J.* **27**, 1824 (1933); **28**, 988 (1934).
18. Muhlethaler, K., *Biochim. et Biophys. Acta* **3**, 15 (1949).
19. Muhlethaler, K., *Biochim. et Biophys. Acta* **5**, 1 (1950).
20. Nanjundayya, C., *Indian Textile J.* **57**, 899 (1947).
21. Reeves, R. E., *J. Biol. Chem.* **154**, 49 (1944).
22. Reid, J. D., Nelson, G. H., and Aronovsky, S. I., *Ind. Eng. Chem., Anal. Ed.* **12**, 255 (1940).
23. Sisson, W. A., *Contribs. Boyce Thompson Inst.* **8**, 389 (1937).
24. Stark, S. M., Jr., *Anal. Chem.* **22**, 1158 (1950).
25. Whistler, R. L., Martin, A. R., and Conrad, C. M., TEXTILE RESEARCH JOURNAL **10**, 449 (1940).

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INDUSTRIAL SECTION

Some Effects of Construction on the Laundering Shrinkage of Wool Fabrics*

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Introduction

Tight, firm structures are generally known to exhibit better dimensional stability in laundering than loose, sleazy materials. The work of Dutton [2, 3] was the first to consider a quantitative approach to the definition of "tightness" and its effect on the shrinkage of knitted fabrics. Recent studies in these laboratories [1] have shown that, entirely aside from the application of a shrink-resistant treatment, appreciable improvement in the laundering ability of knitted woolens may be achieved by increasing the number of stitches per inch or by increasing the weight of the yarns employed. Thus, the density with which the wool is packed into a given area was found to be the chief factor contributing to the resistance to felting. A small improvement in this direction was also found with the use of higher-twist yarns.

It was considered desirable to extend this type of study to woven fabrics as well, in order to obtain some quantitative estimate of the influence of variables of construction on felting on laundering, because such data would have considerable practical utility in the design of fabrics. It was also believed that a wider range of each of the variables could be investigated with woven materials than was possible in the experiments with knit goods.

Since in the previous study of knitted constructions it was found possible to define the tightness for a variety of fabrics in terms of a "cover factor," the relationship between cover factor and feltability of the present fabrics was investigated. The utility of measurements of air permeability and of fabric rigidity in specifying the compactness of a fabric with respect to feltability was also studied.

Materials and Methods

A series of 18 fabrics was hand-loomed from 7 basic commercial yarns, the nominal constructions of which are given in Table I. The fabrics were quite uniform in appearance and were comparable to similar commercially woven materials. The details of construction are given below with the results of measurements of other fabric properties.

Laundering tests were made after relaxation of the fabrics in warm water for 1 hr., hydroextraction, and air-drying. Two successive severe launderings, each comprising a 30-min. washing period at 100°F with low-titer soap as detergent and two 3-min. rinses, were used.

TABLE I. YARNS USED IN WEAVING EXPERIMENTS

Code	Nominal yarn No.	Nominal twist (t.p.i.) Singles	Ply
1	2/12	9.3 Z	6 S
2	2/12	5.9 Z	6 S
3	2/12	14.3 Z	6 S
4	1/6	6.6 Z	—
5	2/7.5	7.5 Z	5 S
6	2/4.2	5.5 Z	3.75 S
7	1/6	6.6 S	—

* This work constitutes a part of the Army Quartermaster program on shrink-resistant wool, which is under the supervision of the National Research Council Advisory Committee on Textile Finishing Research.

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‡ Research and Development Laboratories, Philadelphia Quartermaster Depot, Philadelphia, Pa.

The flexibility of each fabric was estimated by measuring its flexural rigidity by the hanging-heart method of Peirce [6]; a brief description of this method and the appropriate calculations are given by Taylor [10].

Air permeability was measured with the Schiefer device [8] at a pressure drop of 0.5 in. of water. The cover factor, K, was calculated from the relationship: $K = \frac{t}{\sqrt{Y}}$, where t is the number of threads per inch and Y is the effective yarn number. The sum of the warp and filling cover factors is used hereinafter as the measure of tightness.

Results and Discussion

In order to facilitate comparisons, each factor of construction is isolated where possible, and the results are presented separately.

Effect of Fabric Texture

Three plain-woven fabrics were made from identical yarns, varying only the number of ends per inch. The results presented in Table II indicate that substantial increases in felting in laundering occur as the texture is made more open. That is, increasing the weight through the use of more picks and ends results in increased stability. This result is exactly analogous to that found for the knitted constructions in which knitting stiffness (texture) was found to be the most important variable of construction contributing to laundering stability. A similar result was obtained by Johnson [5] with respect to the effect of fabric texture on the milling of woolen fabrics in fulling stocks. While exact correspondence between fulling and felting shrinkage in laundering can hardly be expected, it appears that the influence of fabric texture is at least qualitatively similar in these two types of felting.

Effect of Yarn Twist

The effect of yarn twist on the shrinkage of similar fabrics in laundering is shown in Table III. The results indicate a conspicuous improvement in stability to laundering as the singles twist increases. Fabrics I and J are very closely comparable in all other respects, unequivocally showing the influence of the high-twist yarn in decreasing felting. Fabric A, despite its more open texture, felts somewhat less than fabric I due to the higher yarn twist in the former. The effect of twist on the laundering shrinkage of these woven fabrics is in agreement with that previously reported for knitted fabrics. It appears, however, that moderately high twists are required to achieve this effect to any important degree.

Effect of Plying of Yarns

The felting of fabrics made with single-ply yarns is compared in Table IV with that of fabrics of simi-

TABLE II. FELTING SHRINKAGE OF PLAIN-WOVEN FABRICS IN WHICH NUMBER OF ENDS IS VARIED

Fabric	Yarn No.*	Yarn twist (t.p.i.)*		Fabric weight (oz./yd.²)	Fabric texture (yarns/in.)		Area laundering shrinkage (%)
		Singles	Ply		Warp	Filling	
A	2/11.1	9.2 Z	5.6 S	11.0	31	22	29
B	2/11.1	9.2 Z	5.6 S	9.9	31	16	39
C	2/11.1	9.2 Z	5.6 S	9.2	30	14	46

* Identical yarns were used in warp and filling.

TABLE III. FELTING SHRINKAGE OF PLAIN-WOVEN FABRICS IN WHICH YARN TWIST IS VARIED

Fabric	Fabric texture (yarns/in.)		Fabric weight (oz./yd.²)	Yarn No.	Filling yarn twist (t.p.i.)		Area laundering shrinkage (%)
	Warp	Filling			Singles	Ply	
I	32	26	10.5	2/11.4	5.9 Z	5.2 S	31
A	31	22	11.0	2/11.1	9.2 Z	5.7 S	29
J	31	25	10.9	2/11.4	15.0 Z	5.7 S	23

lar weight and texture made with plied yarns. The data shown for samples PX and A indicate that shrinkage in laundering is similar for these fabrics irrespective of the ply of the yarns.

Another pair of fabrics was available, in which the fabric weights were similar and in which the total number of ends was virtually the same, samples M and C. However, one member of the pair, sample M, was balanced with respect to texture, and, as shown in Table IV, this sample was significantly less feltable than sample C, which had many more yarns in the warp than in the filling direction. This unbalance is seen to affect the magnitude of the flexural rigidity, resulting in a low rigidity value in the direction corresponding to the smaller number of ends. This result suggests that the minimum, rather than the average, value of flexural rigidity can be correlated with the laundering shrinkage of the fabric; this is discussed later in this paper.

With respect to the role of plying, however, with other factors being equal, the use of plied yarns does not confer added shrink-resistance to the cloth. This result is in agreement with the conclusions from the previous study of knitted fabrics [1].

Effect of Direction of Twist of the Yarns

It is well established in the weaving art that the direction of twist of the yarns used will affect the appearance, fullness, and density of the fabric. Thus, Haven [4] noted: "When . . . the yarns are of the same direction of twist, there is a little more tendency to compactness in the fabric than if one thread is of opposite twist from the other." Strong [9] observed that fabrics made with yarns twisted in opposite directions have a fuller feel and show higher air permeability. This arises from the fact that when yarns of similar direction of twist are used for warp and filling, the fibers on the top of the yarn and those on the under surface of a crossing yarn coincide in direction, the yarns "bedding" into one another and resulting in a flatter, more compact fabric. With yarns of opposing twist direction, the warp and filling yarns maintain their integrity to a greater extent, yielding a softer, fuller, and more open cloth. One would expect, therefore, that the latter would be more feltable in laundering. An appropriate comparison of such fabrics is shown in Table V.

Fabric Q, woven from yarns of opposing twist direction, is seen to shrink in laundering to a greater extent than sample N, woven from yarns of similar twist direction, the fabrics being otherwise nearly identical. These samples showed very little difference in flexural rigidity, but the relative compactness revealed by the air-permeability measurements, which are also given in Table V, is in the direction predicted by Strong [9] and does seem to be correlated with the feltability.

TABLE IV. EFFECT OF PLYING OF YARNS ON THE FELTING SHRINKAGE OF PLAIN-WOVEN FABRICS

Fabric	Fabric texture (yarns/in.) Warp	Filling	Total	Fabric weight (oz./yd.²)	Yarn No. Warp	Filling	Area laundering shrinkage (%)	Fabric flexural rigidity (g. cm.) Warp	Filling
PX	27	27	54	10.7	1/5.5	1/5.3	30	.31	.33
A	31	22	55	11.0	2/11.2	2/11.2	29	.42	.37
M	24	21	45	9.7	1/5.3	1/5.3	34	.27	.28
C	30	14	44	9.2	2/11.2	2/11.2	46	.33	.14

TABLE V. EFFECT OF DIRECTION OF TWIST OF THE YARNS ON THE FELTING SHRINKAGE OF 2/2 TWILL FABRICS

Fabric	Fabric texture (yarns/in.) Warp	Filling	Yarn No. Warp	Filling	Yarn twist (t.p.i.) Warp	Filling	Area laundering shrinkage (%)	Air permeability (ft.³/min./ft.²)
N	25	27	1/5.3	1/5.3	5.3 S	5.3 S	41	150
Q	25	26	1/5.5	1/5.3	5.4 Z	5.3 S	48	190

TABLE VI. EFFECT OF YARN NUMBER ON THE FELTING SHRINKAGE OF PLAIN-WOVEN FABRICS OF SIMILAR TEXTURE

Fabric	Fabric texture (yarns/in.) Warp	Filling	Yarn No. Warp	Filling	Fabric weight (oz./yd.²)	Air permeability (ft.³/min./ft.²)	Area laundering shrinkage (%)
B	31	16	2/11.2	2/11.2	9.9	126	39
L	31	17	2/11.2	2/3.9	14.6	56	28
A	31	22	2/11.2	2/11.2	11.0	35	29
K	31	23	2/11.2	2/6.8	13.0	22	26

TABLE VII. EFFECT OF TYPE OF WEAVE ON THE FELTING SHRINKAGE OF FABRICS

Fabric	Fabric texture (yarns/in.) Warp	Filling	Weave	Weight per sq. yd. (oz.)	Area laundering shrinkage (%)	Air permeability (ft.³/min./ft.²)
PX	27	27	Plain	10.7	30	53
Q	25	26	2/2 broken twill	10.6	48	190
H	32	34	3/1 unbalanced broken twill	12.5	20	41
E	33	28	2/2 broken twill	11.8	26	41
F	32	31	2/1 twill	12.4	27	58
D	30	29	2/2 broken twill	11.5	32	76
A	31	22	Plain	11.0	29	35

Effect of Yarn Number

It was considered of interest to compare the felting properties of fabrics of similar textures but made from yarns differing in weight. The data previously given have shown that decreasing the weight through the use of fewer ends results in increased felting shrinkage; in this section a method of changing the fabric weight through the use of different yarn weights, but maintaining the texture, is considered. The comparisons of two such pairs of fabrics is made in Table VI.

The data show that where a large difference in weight is produced by using heavier yarns, a pronounced reduction in felting results. In the comparison between fabrics A and K, the differences in weight are smaller and the fabrics are relatively tight in texture, so that the resulting effect on felting, although in the proper direction, is very small in magnitude. The difference in air-permeability values in these two cases also reflects the laundering behavior, being large where the differences in feltability are also large.

Effect of Type of Weave

Up to this point, consideration has been given to the influence of the yarn-construction variables or of the number of yarns per unit area on the laundering shrinkage of fabrics. It is clear, however, that the manner in which the yarns are interlaced might be expected to affect the fabric feltability. Comparisons of the laundering behavior of fabrics of different weave but otherwise similar, except as indicated, are shown in Table VII.

Of the various weaves tabulated, the plain-woven fabric seems to be relatively felt-resistant. Plain-woven sample PX shrinks much less than does sample Q, a twill weave, although constructionwise the two fabrics are quite similar; the difference in the compactness between these two samples is revealed by the large difference in the air-permeability values. The laundering stability of the plain weave can also be seen in comparing plain-woven fabric A with the twilled fabrics, since sample A is similar to the twills in feltability despite its substantially lower thread count. One would expect that a fabric of such low thread count would be appreciably more feltable than the others in the group. That the plain-weave sample A is as compact as the twills of tighter construction is shown by the similarity in air permeability.

The differences among the various twills with respect to shrinkage are not very great if the texture

TABLE VIII. RELATIONSHIP BETWEEN SHRINKAGE IN LAUNDERING AND VARIOUS MEASURES OF FABRIC COMPACTNESS

Fabric	Shrinkage in laundering (%)			Cover factor			Flexural rigidity (g. cm.)		Air permeability ($ft.^3/min./ft.^2$)
	Warp	Filling	Area	Warp	Filling	Sum	Warp	Filling	
				Plain Weaves					
J	10	15	23	13.1	10.4	23.5	0.49	.39	39
K	12	16	26	13.1	12.5	25.6	.48	1.05	22
L	10	20	28	13.1	12.0	25.1	.39	1.17	56
A	12	19	29	13.1	9.3	22.4	.42	.37	35
PX	16	16	30	11.6	11.6	23.2	.31	.33	53
I	15	19	31	13.6	10.8	24.4	.46	.51	21
M	17	21	34	10.4	9.1	19.5	.27	.28	170
P	18	21	35	10.4	10.4	20.8	.27	.25	160
B	19	25	39	13.1	6.8	19.9	.37	.19	130
C	24	29	46	12.7	5.9	18.6	.33	.14	180
				Twill Weaves					
H	9	12	20	13.6	13.1	26.7	.42	.44	41
E	15	13	26	14.0	11.9	25.9	.44	.32	41
F	14	15	27	13.6	13.1	26.7	.43	.41	58
G	18	16	31	10.6	13.1	23.7	.52	.38	71
D	17	18	32	12.7	12.3	25.0	.41	.34	76
N	23	23	41	10.8	11.6	22.4	.27	.30	150
O	25	23	42	10.8	12.9	23.7	.29	.31	150
Q	26	30	48	10.8	11.2	22.0	.28	.29	190

differences are taken into account. The air-permeability measurements, however, do rate the twill fabrics in approximately the order of their laundering shrinkage.

The data of Johnson [5] bearing on the fulling of woolen fabrics embraced a wider variety of weaves than was available in this study. From his results it can be seen that the float length is an important factor in weave construction with respect to the degree of fulling; other things being equal, fabrics with long-float constructions felt more rapidly and to a greater extent in the fulling stocks. It is not unlikely that a similar, but smaller, effect might be found for felting in laundering if a wider variety of weaves were studied.

Measures of Fabric Tightness

The preceding discussion suggests that the compactness of the fabric structure, whether due to the number or weight of the yarns or to the nature of their interlacing, is the factor which is basic to the feltability of the fabric. It was considered desirable to determine whether a single parameter could be used to describe this tightness or compactness factor. The present study suggests the possible use for this purpose of air permeability, of the flexual rigidity of the fabric, and of the cover factor, the last of which has frequently been used to describe fabric tightness. Table VIII summarizes the measurements of the fabrics with respect to these properties; the relationships between felting shrinkage and cover factor, flexual rigidity, and air permeability are plotted in Figures 1 to 3, respectively.

Since the variation in number of ends or yarn number has been shown to influence feltability, it is not surprising that the cover factor, which is calculated from these construction variables, is also related to the shrinkage in laundering. The graph shown in Figure 1, where shrinkage is plotted as a function of cover factor, indicates a satisfactory over-all relationship. The difference between the two curves suggests that for a given amount of yarn cover, twills are more easily felted than are plain-woven fabrics. This is a reasonable result in view of the greater float length in twills and, consequently, a longer segment of yarn between tie-down points. This result is in agreement with the previous discussion on the effect of weave.

The flexural rigidity of the fabrics is also affected by a number of the same elements as cover factor, and Peirce [7] noted that as the cover factor of a fabric increases, it becomes increasingly stiff and

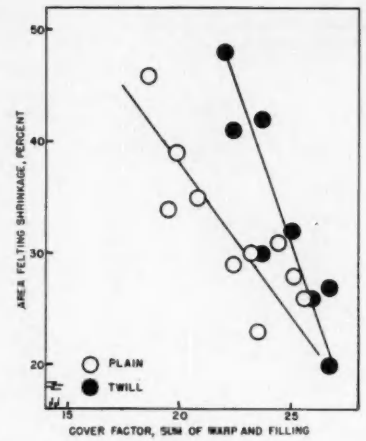

FIG. 1. *The relationship between the felting shrinkage in laundering and the cover factor of plain- and twill-woven fabrics.*

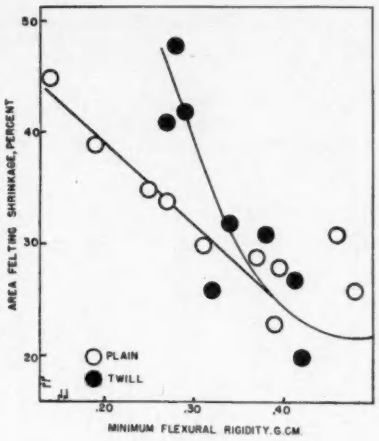

FIG. 2. *The relationship between the felting shrinkage in laundering and the flexural rigidity of plain- and twill-woven fabrics.*

hard. The inverse relationship between laundering shrinkage and flexural rigidity for the present fabrics is plotted in Figure 2. The lower value of rigidity was used in each case, irrespective of whether it was that for the warp or filling direction, this procedure being suggested by the data given previously.

The curves in Figure 2 describe a generally satisfactory relationship for these samples between felting behavior and ease of deformation of the fabric. This figure again demonstrates the relatively high feltability of twills compared to plain-woven fabrics, the shrinkage-rigidity curve for the twills falling appreciably above that for the plain-weave fabrics.

The relationship between the felting shrinkage and the air permeability of the various fabrics is plotted in Figure 3. The air permeability, which is descriptive of the fabric compactness, shows a fairly good relationship to laundering shrinkage.

Each of these parameters—cover factor, flexural rigidity, and air permeability—appears to be related to the feltability of a fabric, and may be considered to be a measure of fabric tightness. Cover factor and flexural rigidity are interdependent to some extent, and their magnitudes are affected by the yarn diameter and the number of yarns present.

When the yarns are interlaced in different ways, however, as by variation in weave or in twist direction of the yarns, the difference in construction of the resulting fabric may not be revealed by cover factor or rigidity measurements. In such cases, air

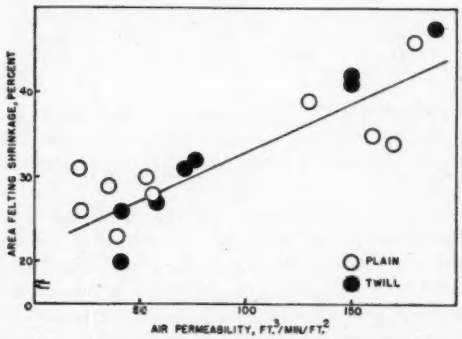

FIG. 3. *The relationship between the felting shrinkage in laundering and the air permeability of plain- and twill-woven fabrics.*

permeability may be used as a measure of the compactness with respect to felting.

The case in which the amount of twist in the yarn influences feltability differs from those just discussed, in that the use of high-twist yarns decreases shrinkage in spite of the fact that such fabrics are more open. Fiber migration is hindered in the high-twist yarn, so that feltability is lower in spite of the apparent openness of the fabric.

Since it is generally agreed that felting occurs as a result of the tendency of the individual fibers to migrate relative to one another, the reasons for the various construction factors operating in the way

they do is clear. For a given amount of relative fiber movement, high values of yarn twist and the use of weaves in which the yarns are bound at frequent intervals by the cross-yarns obviously will require the input of more energy in the laundering operation in order to overcome the higher frictional forces. Similarly, in situations in which there are many fibers per unit area, the normal forces exerted on each fiber are relatively large, again resulting in increased frictional forces between fibers.

Summary and Conclusions

1. Greater stability to felting shrinkage in woven fabrics may be achieved through the use of a larger number of ends per inch, higher-twist yarns, and heavier yarns (lower yarn number).

2. The use of plied yarns, other things being equal, does not appear to confer added shrink-resistance to a fabric.

3. A fabric woven with warp and filling yarns of opposite twist direction felts to a greater extent than one in which the yarns are of the same direction of twist.

4. Plain-woven fabrics show greater felt-resistance than various twill weaves of similar texture.

5. In general, the relative feltability of a fabric is determined by its compactness; appropriate measures of the latter for this purpose are cover factor, flexural rigidity, and air permeability.

Literature Cited

1. Bogaty, H., Weiner, L. I., Sookne, A. M., and Harris, M., TEXTILE RESEARCH JOURNAL **21**, 102 (1951).
2. Dutton, W. A., *J. Textile Inst.* **37**, P212 (1946).
3. Dutton, W. A., *J. Textile Inst.* **40**, P638 (1949).
4. Haven, G. B., "Mechanical Fabrics," New York, John Wiley & Sons, 1932.
5. Johnson, A., *J. Textile Inst.* **29**, T7 (1938).
6. Peirce, F. T., *J. Textile Inst.* **21**, T377 (1930).
7. Peirce, F. T., *J. Textile Inst.* **28**, T45 (1937).
8. Schiefer, H. F., and Boyland, P. M., *J. Research Natl. Bur. Standards* **28**, 637 (1942).
9. Strong, J. H., "Fabric Structure," Brooklyn, Chemical Publishing Co., 1947.
10. Taylor, H. M., *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland* **1945**, p. 13.

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Fundamentals of Flame Retardancy*

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Contribution from the Experiment Station, Hercules Powder Company, Wilmington, Delaware

BEFORE considering the reactions occurring in the burning of textile fabrics and the mechanisms by which these combustive processes can be retarded, it would be well to review briefly the relationships between the terms "burning," "combustion," and "flaming." "Burning" may be defined as "the process of uniting chemically with oxygen so rapidly as to produce heat and light." The act of burning has been termed "combustion." When the material undergoing active combustion is gaseous in nature, the resulting heat and light generated are manifested in the phenomenon of "flaming"—*i.e.*, flaming is exhibited by gas-phase oxidation reactions. When, on the other hand, a solid material is actively involved in the combustion reaction, it may become incandescent as a result of the heat evolved, but the burning is not attended by the development of flame. The flames which appear in the combustion of solid fuels such as wood, coal, or textile fabrics are really evidence of the combustion of gaseous products distilled from the fuel by heat. The purpose of the present review is to clearly differentiate between the two types of active combustion—gas-phase reactions (flaming), and direct reactions between solid fuels and oxygen (glowing).

For illustrative purposes, these two isolated phenomena of the combustion of textile fabrics may be compared with the burning characteristics of coal and coke. The fuel value of coal is dependent primarily upon its carbon content. Part of the carbon present, however, is termed "fixed carbon," in that it cannot

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be volatilized on pyrolysis, while part is combined with hydrogen and nitrogen in the form of volatile (and flammable) hydrocarbon compounds. Volatile matter varies widely, from less than 6% for anthracite to 40% to 60% for cannel coal. In burning, the volatile hydrocarbon constituents are distilled from the solid phase and combine with oxygen in the gaseous phase, resulting in flaming combustion. A cellulosic fabric compares with cannel coal in its content of volatile, flammable, hydrocarbon components, and it exhibits the same flaming combustion on burning. Once the flaming reaction has consumed a portion of the fabric, however, a charred fabric residue may remain, which can continue to oxidize through an incandescent oxidation of the carbon char. Since all volatile components have already been evolved, this glowing combustion represents a solid-gas reaction between the char and the oxygen of the air. This latter reaction is analogous to the burning of coke, where the absence of flammable volatile constituents results in a flameless, glowing combustion reaction. Although "flaming" and "glowing" reactions may occur almost concurrently when a fabric burns, the two phenomena involve very different oxidation reactions and must be considered independently when studying the function of combustion inhibitors. Actually, examples can be cited of glow retardants which exert little effect on the flaming combustion of fabrics and of highly effective flame retardants which have no effect on, or may actually intensify, afterglowing tendencies. This general picture of the combustion reactions suggests several approaches to preventive mechanisms. Since the bulk of available fundamental data on the combustion of fabrics is based on studies of cotton and rayon fibers, the present discussion is aimed exclusively at cellulosic textiles. In many cases, the generalizations involved can be extended to include various synthetic fibers.

General Preventive Measures

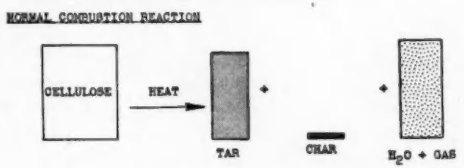
In the combustion of a textile fabric, or similar fuel, flaming occurs only at the gas-air interface where oxidation can occur. All heat of reaction is generated here also. The prevention of flaming then may be achieved by the addition of compounds capable of *reducing the amount* of flammable decomposition products or *inhibiting their diffusion* into the surrounding atmosphere where oxidation may occur. Such compounds could function by many mechanisms, such as: exclusion of oxygen; decrease in the diffusion rate of oxygen or fuel products; inhibition of reactions leading to fuel formation; inhibition of exothermic reactions; dissipation of heat formed.

In the discussions of the specific mechanisms which follow, no attempt is made to consider the multitude of retardant compositions available in terms of their methods of functioning. This has been covered in some detail in previous publications [3]. Instead, preferred mechanisms will be considered, making use of the simplest borate- and phosphate-type inhibitors.

Flaming Combustion

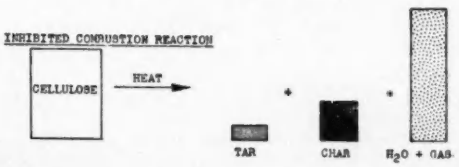
The reactions occurring during flaming can be divided into primary and secondary reactions. The primary reaction may be considered as the thermal degradation of the fabric attended by distillation of volatile decomposition products. The secondary reaction involves the oxidative combustion of decomposition products accompanied by the evolution of heat and light.

Available data indicate that flame retardants are effective primarily by inhibition of the primary reaction of degradation and distillation. When thermally degraded at high temperatures, cellulose breaks down into three major phases: a solid char, a volatile liquid of tarry nature, and a gaseous fraction.



It would seem that the occurrence of a flaming reaction would be dependent upon the relative amounts of these phases formed and perhaps the rates of formation. Such has been shown to be the case.

Since flaming is essentially the rapid oxidation of a combustible vapor, effective flameproofing should be accomplished by retaining the degradation prod-



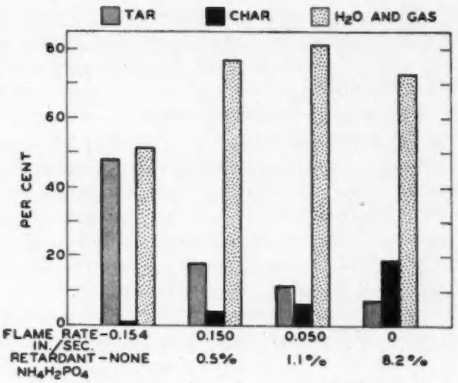


FIG. 1. *Effect of retardants on products of fabric combustion.*

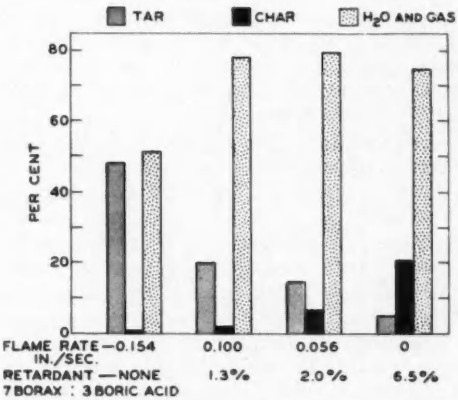


FIG. 2. *Effect of retardants on products of fabric combustion.*

ucts in the solid phase. The ideal case would then be represented by the reaction:

$$(C_6H_{10}O_5)_n \rightarrow 6nC + 5nH_2O$$

Actually, the addition of an effective retardant to cellulose greatly increases the amount of char formed on thermal degradation. (See reaction at bottom of p. 902.)

Furthermore, the effect has been clearly shown to be proportional to the actual flameproofing efficiency of the retardant added. The effects of the addition of increasing amounts of ammonium phosphate on the thermal decomposition products of cellulose are shown in Figure 1. The reduction in tar formation

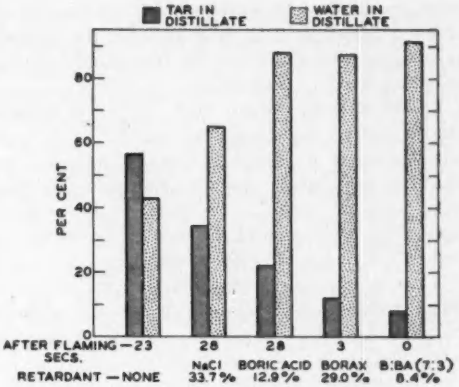


FIG. 3. *Retardations of tar formation during fabric combustion.*

and the increase in charred residue are paralleled by a corresponding decrease in flammability. Dry gases formed do increase in amount and rate of formation but remain essentially constant in composition. Furthermore, unlike the tar and char variations, the effect on the gaseous fractions is not specific for retardant materials. As seen in Figure 2, virtually the same effects are obtained by the use of a borax-boric acid mixture. The similarity in the behavior of these two retardants is particularly significant since they are believed to function via two different basic mechanisms.

The principal effect of an efficient flame retardant, then, appears to be its influence on the primary degradation reaction via reduction in the amount of combustible tarry products and a corresponding increase in the amount of solid char formed. This is in agreement with the ideal reaction mentioned previously. One more factor which must be considered, however, is the amount of water formed, as indicated in the same reaction. When actually evolved, the tarry products are accompanied by appreciable quantities of water. At the same time the amount of dry tar is reduced as a result of the retardant action, the amount of water evolved is appreciably increased. Therefore, the effectiveness is due not only to a reduction of fuel supply but also to a dilution of the combustible vapors with water. This is clearly shown in Figure 3, wherein the percentage of tar in the distillate is shown to closely parallel the afterflaming tendency. With the addition of retardants of increasing efficiency, the amount of tar in the con-

densable distillate is decreased and the amount of water increased until, at about 12% tar, the distillate is no longer flammable and the combustion reaction is extinguished for lack of fuel.

It was deemed possible that part of the effects shown were attributable to differences in the chemical composition of the tarry products. Studies of the chemical and physical characteristics of these products, however, showed no variations in the composition which would contribute appreciably to the observed differences in performance.

Thus far we have considered only the effects of flame inhibitors on the thermal degradation products of cellulose, without regard to the mechanisms by which these effects are accomplished.

Many theories have been proposed to explain the phenomenon of flame-resistance. Some are much more firmly based on experimental data than others. Some flameproofing salts and mixtures have been shown to function primarily by physical mechanisms. These materials are generally highly hydrated salts of fairly low melting point or mixtures of a hydrated compound and a low-melting salt. The mechanism appears to be the melting of the compound or mixture, followed by the formation of a stable, solid foam formed by the evolution of decomposition products. The foam serves as a barrier between the fabric and the flame, affording thermal insulation and also entrapping combustible, tarry degradation products and causing them to be further degraded to the gaseous and solid phases. Mixtures of borax and boric acid are representative of this type. In some cases it has been proposed that a thick coating is formed around each fiber or thread, thus serving the same function. In the case of a continuous solid film, it is probable that add-ons would necessarily have to be quite high.

Two credible theories have been advanced to explain the phenomenon of flame-resistance on the basis of a chemical relationship with the fiber. In the case of inorganic acids and their acid salts, using ammonium phosphate as an example, the mechanism has been regarded as primarily chemical in nature. The data available indicate the promotion of the decomposition of cellulose in the direction of solid char and water. One interpretation of this is the existence of a catalytic dehydration reaction. This is supported by the efficiency of this class of materials at relatively low add-ons and the slight additional effect of much greater amounts of added retardant. Such an interpretation is also in line with the observed pyrolysis and combustion data. The acid anhydride formed at combustion temperatures is visualized as promoting the formation of water through its strong dehydrating action. It is further theorized that the attracted water is subsequently released, regenerating the anhydride for continuous functioning. Such a mechanism is in agreement with the strong dehydrating action of the anhydrides, using phosphoric anhydride as an example, and is supported further by the fact that no flameproofing properties are displayed in cases where the salt is incapable of liberating the acid residue on heating.

The same phenomena can be interpreted in different terms on the basis of hydrogen-bonding energies. The majority of flameproofing agents of this type are materials possessing high hydrogen-bonding activity. Knowing that the observed effect is a retention of decomposition products in the solid state, the formation at flame temperatures of a residue capable of attracting and holding adjacent cellulose chains appears to agree well with the facts. Normally, water molecules may be pictured as serving in the capacity of cross-linkages between adjacent cellulose chains. At flame temperatures, the water molecules are volatilized, permitting cellulose to be thermally degraded into relatively small fractions which contribute to the combustible tarry vapors. The partial replacement of water in this case by materials having strong hydrogen-bonding properties, which at the same time are not volatile at flame temperatures, promotes continued interlinkages even at extremely high temperatures. The resulting increase in the average size of fragments formed would be expected to result in the observed increase in solid residue at the expense of volatile tarry vapors.

Some flameproofing materials can not as yet be assigned to either of the two preceding categories. When more is known of their performance at elevated temperatures in the presence of cellulose, they may show more apparent similarities. For the present, many carbonates and ammonium salts, as examples, are believed to function by the evolution of large quantities of noncombustible vapors. The evolution of appreciable amounts of incombustible gases or sublimate is claimed to dilute the combustible atmosphere surrounding the fibers. Although it is entirely possible that such a mechanism does contribute to the over-all effect, there is no appreciable evidence to indicate that this should be considered one of the primary causes of flameproofing action. It should be borne in mind, however, that any one

retardant may well function by more than one of the mechanisms suggested. In fact, this is probably the case in most instances.

Glowing Combustion

The glowing combustion encountered with charred fabrics may be compared in many respects with the combustion of coke or similar pyrolyzed forms of carbon. The charred fabric may be regarded as a bed of solid fuel constituted of a group of particles, predominantly carbon, which in active combustion undergo surface oxidation at high temperatures (600°–700°C). The mechanism attributed to this combustion reaction involves a two-stage consumption of oxygen [2]:

Primary reaction (solid-gas): $C + \frac{1}{2}O_2 \rightarrow CO$
Secondary reaction (gas phase): $CO + \frac{1}{2}O_2 \rightarrow CO_2$

It is pertinent that whereas the primary reaction involves the liberation of 26.43 kcal./mol. as the heat of formation of CO, the secondary reaction liberates 67.96 kcal./mol., nearly 2.5 times as much heat, in the combustion of CO to CO_2. As will be discussed in some detail below, glow retardants exert their maximum effect in inhibiting the secondary reaction, the primary reaction occurring in the presence of even the most potent inhibitors.

In studies of the glowing tendencies of fabrics, relatively few compounds or compound types have been found which exhibit significant influence on the afterglow phenomenon. For all practical purposes, effective compounds are limited to the thermolabile borates and phosphates. The efficacy of these materials and the mechanisms by which they are believed to function will be treated in some detail below.

A second class of compounds, including inorganic silicates and certain organic polymeric resins, is also effective, although to a much lesser extent. The effectiveness of these materials may be attributed to the shielding of the carbon filaments from oxygen via the formation of a protective film barrier. In any event, their effectiveness is of an entirely different order than that of the borates and phosphates.

The effect of glow inhibitors may be shown clearly by pyrolyzing treated and untreated fabric swatches in an inert atmosphere and then examining the resulting chars for their afterglowing tendencies. In one series of experiments [4] fabric specimens were thermally degraded in an atmosphere of nitrogen at 350°C and subsequently were tested in air for glowing characteristics, noting loss of weight during pyrolysis, loss of weight during exposure of char to flame, and duration of glowing period on removal from the igniting flame.

Representative data are shown in Table I. It may be seen that the addition of an inert material like sodium chloride has relatively little effect upon the isolated glowing reaction, while borax and the sulfamate actually increase glowing tendencies. The latter effect can be explained partially by the presence of much greater amounts of char after pyrolysis. Boric acid and ammonium phosphate both exert a powerful influence on both the duration and the extent of the glowing reaction, as little as 0.5% of the latter almost completely inhibiting flameless combustion.

As is indicated by the relative behavior of borax and boric acid, all borates and phosphates are not effective in retarding afterglow. A convenient example of the differences encountered may be found with orthophosphoric acid and its sodium salts, as presented in Table II. As indicated in those compounds where the acid anhydride is balanced by the presence of an equivalent amount of alkali or alkaline-earth oxide, no glow-inhibiting properties are obtained. Only when the salt will decompose at flame temperatures or below, yielding an acid residue, is it capable of inhibiting the glowing reaction.

TABLE I. RETARDATION OF GLOWING OF CHARRED COTTON FABRIC

Retardant	Add-on (%)	Weight loss during pyrolysis (%)	Weight loss by glow (%)	Glowing time (sec.)
None	0	79.5	18.8	73
Sodium chloride	10	67.0	8.6	62
Ammonium sulfamate	10	54.0	37.7	360
Borax	10	60.0	27.4	180
Boric acid	10	54.5	1.5	0
Ammonium dihydrogen phosphate	0.5	68.9	3.1	9
	10	55.2	0.2	0

TABLE II. RELATIVE GLOW RETARDANCY OF ALKALI PHOSPHATES (COTTON FABRIC, 45° MICROBURNER FLAME TEST)

Retardant	Add-on (%)	After-glow (sec.)	Char area (sq. in.)
$Na_3PO_4 \cdot 12\ H_2O$	77.5	400	CC*
$Na_2HPO_4 \cdot 12\ H_2O$	57.4	70	CC*
$NaH_2PO_4 \cdot H_2O$	16.9	0	2.4
H_3PO_4	14.8	0	2.5

* CC = Completely consumed by afterflaming and afterglow.

Evidence of the mechanism by which the thermolabile phosphates and borates retard the oxidation of charred fabric residues has been obtained by a study of the composition of reaction products. By thermally degrading fabric specimens in an inert atmosphere and then oxidizing them under identical conditions in a standard "combustion train," a study was made of the effect of additives on the products of carbon oxidation. A temperature of 500°C and air-flow of 200 cc. per min. were found to be high enough to produce an oxidation reaction unaffected by further increases in temperature or air supply. Under these conditions, the addition of as little as 1% diammonium phosphate reduced the amount of CO_2 evolved from 2.5 g. per gram of char for the untreated fabric to about 0.8 g., and this effect was not altered significantly by further additions of the phosphate. Boric acid was also effective in reducing CO_2 formation, although inferior to the phosphate. In conjunction with the decrease in the amount of CO_2 evolved, a corresponding increase in the amount of CO formed was noted. A typical set of data is shown in Table III. Considering fabric residues which had been pyrolized for 30 min., the addition of 5% $(NH_4)_2HPO_4$ reduced the amount of CO_2 formed from approximately 2.4 g. to about 1.2 g., CO formation increasing from 0.29 g. to 1.1 g. For untreated fabric the molar ratio of CO_2/CO in exit gases is 5.2, whereas the addition of 5% diammonium phosphate to the original fabric decreases this ratio to 0.7. This effect on the gaseous oxidation products is not shown by materials which do not possess glowproofing properties.

It will also be noted from this data that the time of pyrolysis is a very important factor. The longer the fabric has been pyrolyzed, or the more completely it has been converted to a pure carbon structure, the greater the effect exhibited by the oxidation inhibitor. Apparently, the presence of hydrocarbon residues or residual water decreases the effectiveness of the combustion inhibitor.

This evidence, then, based on studies of the combustion of untreated and treated cotton fabrics, indicates inhibition of glowing combustion by means of a catalytic effect on the course of the oxidation of carbon. In the preferential formation of CO, rather than CO_2, a reaction of lesser exothermicity results, since the heat of reaction is reduced from 94.4 kcal./mol. to 26.4 kcal./mol. Apparently, when the principal oxidation product is CO, the heat produced is insufficient to support a self-sustaining glowing reaction.

Confirmation and clarification of these observations has been found in similar studies of the effect of various reagents on the oxidation reactions in the combustion of coke. Arthur and Bowring [1] examined the effects of various inhibitors on the oxidation of several carbonaceous materials, including electrode carbon, wood charcoal, graphite, and coke. The retardants tested included Cl_2, CCl_4, $SnCl_4$, SO_2, HCl, $POCl_3$, and P_2O_5. In their experiments a carbon tube was burned inside a quartz tube which was held in a furnace at 850°C. The carbon tube was brought up to temperature in a stream of nitrogen and was then burned in a dry-air stream. Inhibitors were added to the dry-air stream in vapor form. Obviously, with such a technique inhibitors could be studied which are entirely impractical from

TABLE III. EFFECT OF $(NH_4)_2HPO_4$ ON OXIDATION OF CHARRED FABRICS

Pyrolysis time (min.)	Combustion products: Grams of CO_2 from combustion		Grams of CO from combustion		Molar ratio (CO_2/CO)	
	Untreated	5% DAP*	Untreated	5% DAP*	Untreated	5% DAP*
10	2.29	2.09	0.252	0.472	5.78	2.82
15	2.42	1.70	0.256	0.585	6.03	1.85
20	2.60	1.55	0.210	0.833	7.88	1.19
30	2.42	1.16	0.294	1.10	5.24	0.67

* DAP = Diammonium phosphate.

the standpoint of their retardation of afterglow in textile fabrics, where the inhibitor must be sufficiently nonvolatile to remain on the fabric throughout exposure to the igniting flame.

An example of the results obtained in this work is shown in Figure 4, the inhibitor in this case being

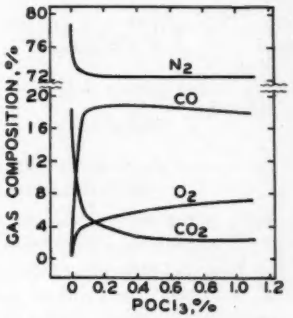


FIG. 4. *Effect of $POCl_3$ on oxidation products* [1].

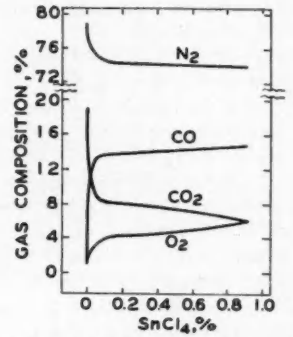


FIG. 5. *Effect of $SnCl_4$ on oxidation products* [1].

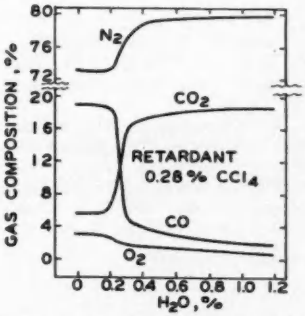


FIG. 6. *Effect of H_2O on inhibiting action* [1].

$POCl_3$. In the normal combustion, exit gases are predominantly CO_2, while the addition of 0.2% to 1% inhibitor produces large increases in the CO concentration at the expense of the CO_2 content. The same behavior is shown for $SnCl_4$ in Figure 5, although the latter is somewhat less effective than $POCl_3$. In general, Arthur and Bowring found that all of the materials added increased the CO/CO_2 ratio in the combustion gases, although they varied considerably in their effectiveness. The phosphorus halides were the strongest inhibitors found. The changes in CO/CO_2 ratio noted occurred with less than 1% additive in all cases, and greater amounts of additives had no effect. Another interesting comparison is found in their report that the presence of H_2O- or H_2-containing materials tended to reverse the trend of the CO/CO_2 ratio. This is shown in Figure 6, the inhibitor in this case being CCl_4. The presence of small amounts of water served to effectively nullify the inhibiting effect of the added retardant. The same phenomenon is illustrated by the effect of incomplete pyrolysis of treated fabric swatches, as was shown in Table III. As indicated earlier, considering the two-stage oxidation reactions of carbon:

$$\text{Primary reaction: } C + \tfrac{1}{2}O_2 \rightarrow CO \text{ (solid-gas)}$$
$$\text{Secondary reaction: } CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \text{ (gas phase)}$$

the majority of the inhibiting effect was aimed at the secondary reaction. There was no evidence that the primary reaction was different when retardants were absent or present.

In considering the mechanism of this inhibiting action, both dry and wet reactions must be considered in the ignition of carbon monoxide-oxygen mixtures. When the system has been exhaustively dried, the reaction is principally the dry one, as represented by the secondary reaction above. When hydrogen-containing species are present, however, the wet reactions occur, probably originating from the water-gas reaction:

$$CO + H_2O \rightarrow CO_2 + H_2.$$

In this case, H_2O is re-formed by the combination of H_2 and O_2, resulting in a branching chain reaction. What the links in the chain reaction are depends upon the kinetics of the reaction of hydrogen and oxygen, but the links are produced mainly from H_2O present or from the hydrogen content of the carbon. Inhibition of the oxidation of CO must be

due to a reaction between the retardant or its degradation products and one of the links in the chain reaction to give a stable product. The fact that very small quantities of retardant effectively inhibit the gas-phase oxidation of CO is not surprising in view of Arthur and Bowring's estimate that the presence of 1 water molecule can lead to the oxidation of at least 500 CO molecules. Substances with high water affinity would be expected to influence the chain reaction, inhibiting the exothermic oxidation of CO and increasing the CO/CO_2 ratio in exit gases, since they would compete with CO for H_2O molecules:

$$P_2O_5 \xrightarrow{H_2O} 2HPO_3$$

$$B_2O_3 \xrightarrow{H_2O} H_2B_4O_7$$

$$SO_3 \xrightarrow{H_2O} H_2SO_4$$

In the case of halogenated compounds, the elemental halogens formed by pyrolysis may be presumed to inhibit the oxidation reaction by suppressing the concentration of chain links such as H_2, which are essential to the branching chain reaction. These materials are much less effective than the phosphate type, Arthur and Bowring having found that as little as 0.2% H_2O in the gaseous system largely destroys the inhibiting effect.

The efficiency of a retardant would depend upon the speed of reaction with chain links, the position of the link destroyed in the reaction chain, and the stability of the product formed. Since the inhibitors with high water affinity react rapidly, remove H_2O molecules at the beginning of the reaction chain, and form relatively stable products, their high efficiency is to be expected.

The relative stability of the end-products formed may serve to explain the scarcity of glow inhibitors of this type and the outstanding performance of thermolabile phosphates, phosphites, and phosphonates. Considering ammonium sulfate, borate, and phosphate, which increase in effectiveness in that order, the following reactions illustrate the relative stability of the end-products of combination of the acid anhydride with H_2O:

$$\underset{\text{Sulfuric}}{H_2SO_4} \xrightarrow{150°\text{–}180°C} SO_3 \uparrow + H_2O \uparrow$$

$$\underset{\text{Orthoboric}}{2H_3BO_3} \xrightarrow{80°\text{–}100°C} \underset{\text{Metaboric}}{2HBO_2} + 2H_2O \uparrow$$

$$4HBO_2 \xrightarrow{167°C} \underset{\text{Tetraboric}}{H_2B_4O_7} + H_2O \uparrow$$

$$H_2B_4O_7 \xrightarrow{276°C} 2B_2O_3 + H_2O \uparrow$$

$$\underset{\text{Orthophosphoric}}{2H_3PO_4} \xrightarrow{225°C} \underset{\text{Pyrophosphoric}}{H_4P_2O_7} + H_2O \uparrow$$

$$H_4P_2O_7 \xrightarrow[800°\text{–}900°C]{\Delta \text{ slowly up to}} \underset{\text{Metaphosphoric}}{2HPO_3} + H_2O \uparrow$$

$$HPO_3 \xrightarrow{\Delta} \text{Vaporizes at } 850°\text{–}950°C \text{ without decomposition}$$

On this basis, phosphoric anhydride would be much more effective in removing H_2O molecules from the combustion gases and preventing their return into the exothermic oxidation reaction than would boric or sulfuric anhydrides. This is substantiated by studies of the combustion products of carbon oxidation and also by practical tests of the glowing tendencies of treated cotton fabrics.

The influence which H_2O- and H-containing species exert in catalyzing the exothermic oxidation of CO and nullifying the inhibiting effect of added retardants at least partially explains: (1) the fact that only the best glow inhibitors are effective in charred fabric systems (where moderate quantities of H_2O and H are always present); and (2) the relative unimportance of the inhibition of the $CO \rightarrow CO_2$ reaction as a factor in the prevention of flaming combustion, where enormous quantities of H_2O and hydrocarbon molecules are injected into the gas phase by the thermal degradation of the fabric.

Literature Cited

1. Arthur, J. R., and Bowring, J. R., *J. Chem. Soc.*, Supp. Issue No. 1, pp. S1–12 (1949).
2. Bangham, D. H., and Thring, M. W., *Coal Research*, p. 48 (Sept. 1944); *Trans. Faraday Soc.* **42**, 376 (1946).
3. Little, R. W., "Flameproofing Textile Fabrics," A. C. S. Monograph No. 104, New York, Reinhold Publishing Corp., 1947.
4. Little, R. W., "Flameproofing Textile Fabrics," A. C. S. Monograph No. 104, New York, Reinhold Publishing Corp., 1947, pp. 65–8.

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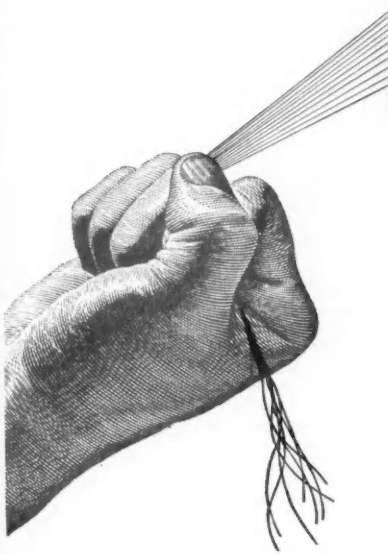

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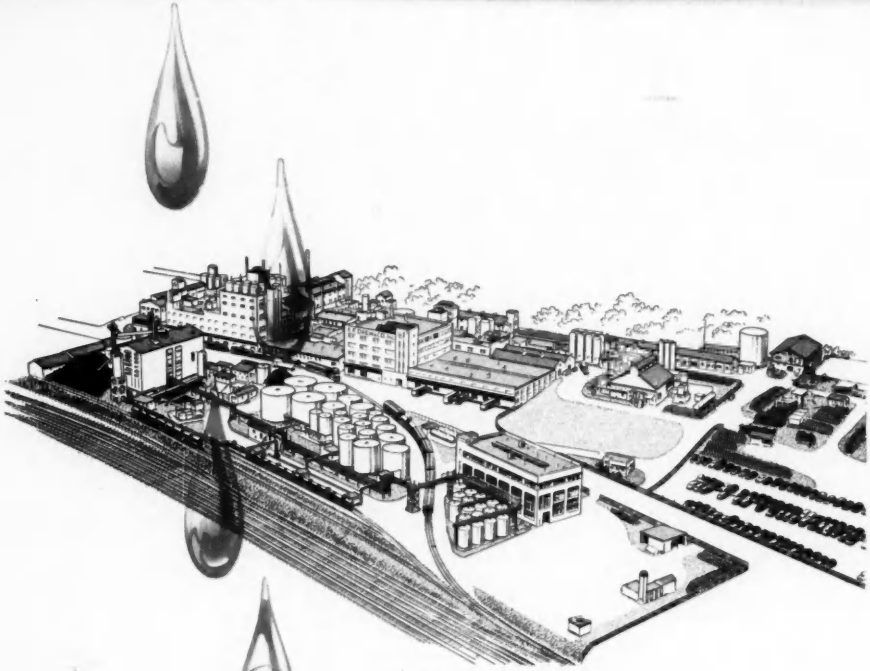

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